

UNCLASSIFIED

---

AD 400 734

*Reproduced  
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY  
ARLINGTON HALL STATION  
ARLINGTON 12, VIRGINIA



---

UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

63-3-1

Document No. ARA-T-9159-2

**SUMMARY REPORT NO. 2**

**STUDY OF MATERIALS FOR THERMIONIC CONVERTERS**

BY

**HAROLD HOMONOFF  
STANLEY RUBY**

**ARACON LABORATORIES  
CONCORD, MASSACHUSETTS**

A DIVISION OF ALLIED RESEARCH ASSOCIATES, INC.

31 DECEMBER 1962

**OFFICE OF NAVAL RESEARCH**

**CONTRACT No. Nonr-3385(00)  
TASK No. NR 099-355**

APR 9 1963  
U.S. NAVY

Reproduction in whole or in part is permitted for any  
purpose of the United States Government

400 734  
CATALOGED BY ASTIA 400 734  
AS AD No. \_\_\_\_\_

**Document No. ARA-T-9159-2**

**SUMMARY REPORT NO. 2**  
**STUDY OF MATERIALS FOR THERMIONIC CONVERTERS**

**BY**  
**HAROLD HOMONOFF**  
**STANLEY RUBY**

**ARACON LABORATORIES**  
**CONCORD, MASSACHUSETTS**  
**A DIVISION OF ALLIED RESEARCH ASSOCIATES, INC.**

**31 DECEMBER 1962**

**OFFICE OF NAVAL RESEARCH**

**CONTRACT No. Nonr-3385(00)**  
**TASK No. NR 099-355**

Reproduction in whole or in part is permitted for any  
purpose of the United States Government

## ABSTRACT

This program has been concerned with an examination of the fundamental properties of materials from a solid-state physics and chemistry point of view. In this report particular attention has been laid to the factors which influence the work function and its temperature coefficient for metals, semiconductors, and insulators. Considerable emphasis was placed upon the surface properties of solids and upon the manner in which the surface barriers and adsorbed monolayers affect the total work functions. Both internal and external work functions were considered. Tables were compiled of published adsorption data, and of properties of certain photoemitters which are potentially useful as low work function collectors in thermionic converters.

## TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	ii
SECTION 1 INTRODUCTION	1
SECTION 2 TEMPERATURE COEFFICIENT OF WORK FUNCTION OF METALS	2
SECTION 3 TEMPERATURE COEFFICIENT OF THE WORK FUNCTION FOR SEMICONDUCTORS	14
a. Temperature Coefficient of the Fermi Level	14
b. Approximations - Fowler Equation	20
c. Possible Mechanism of Oxide Coated Cathode	23
SECTION 4 EFFECT OF ADSORBED LAYERS ON THE WORK FUNCTION OF SOLIDS	30
a. Introduction	30
b. Physical Adsorption	30
c. Chemisorption	36
d. Importance of Crystallographic Planes	46
e. Adsorption Data	47
SECTION 5 LOW WORK FUNCTION MATERIALS	60
SECTION 6 SUMMARY	68
REFERENCES	70
ACKNOWLEDGEMENT	78

## 1. Introduction

This program has been concerned with the study and predictions of classes of materials, and of individual materials which show promise for utilization as one of the components of a thermionic energy converter. At the same time, it is concerned with the identification of those material classes which show little promise for such utilization.

In the first summary report (14) studies were made of the underlying structural causes which determine the values of such material properties as work function, electron affinity, vapor pressure, thermal conductivity, etc. Particular attention initially was given to Alkaline earth oxides, transition metalloids, rare earth hexaborides, and the internal work functions of semiconductors.

In this summary report No. 2, emphasis is placed on a study of the solid state and structural properties of metals and semiconductors, and the factors which mainly affect their total work function and its temperature coefficient.

Information is presented concerning the contributions of individual crystallographic planes to the total work function of a polycrystalline material.

The thermionic constants of emitters and collectors are known to be critically dependent upon the environment in which they operate. An investigation, therefore, was initiated of the electronic interactions involved and the changes in work function which can be expected as a result of adsorption on a surface of partially complete monomolecular films. The future possibility of closely controlling the properties of surfaces to obtain desired results is indicated.

## 2. Temperature Coefficient of Work Function of Metals

It is usually considered that the electron current densities obtained from emitters, which may be predicted by the Richardson-Dushman equation, is identified with thermionic emission as measured by the usual laboratory methods. The validity of this equation has been substantiated from a generalized thermodynamic argument and from quantum mechanics; thus

$$J_{\text{sat}} = \frac{2 (2\pi m k T) k T}{h^3} \exp - [\phi / k T]$$

where  $\phi$  = the work function in ev.  
 $m$  = effective mass of an electron  
 $k$  = Boltzmann's constant  
 $h$  = Planck's constant

The first part of this equation may be recognized as the familiar Richardson A constant where  $A = \frac{4\pi m k^2 e}{h^3} = 120 \text{ amp/cm}^2 \text{ deg}^2$ . However, the following three aspects of thermionic measurements stand in the way of the direct use of the Richardson-Dushman equation:

1. The true work function is dependent on the temperature.
2. The theoretical evaluation of current density is seldom correct because of surface inhomogeneities (Patch effect).
3. The observed energy distribution of the emitter electrons is not found to be that predicted by the equation.

In the discussion to follow, it will be mainly the first aspect that will be considered; the patch effect will be studied in detail later. With regard to the third aspect, it will suffice to state that two different explanations have been offered for this particular behavior. The phenomenon may either be caused by a reflection effect at the surface, or else the experimental results depend on the assumption that as electrons are emitted, the degree that the quantum states (as defined in the band theory of solids) are filled may be changed somewhat in the region near the surface. Thus, when the number of electrons capable of escape is reduced at the surface, a deficiency in slow electrons may result. The "true" work function of a solid,  $\phi_t$ , may



be defined as the difference in energy between the Fermi level within a material and the vacuum level outside the surface of the material.  $\phi_t$  may also be expressed as the difference in energy between the total potential barrier or electron affinity,  $\chi$ , at a surface (energy difference between the bottom of the conductor band and an electron at rest at infinity) and the Fermi level  $E_f$  (which is the difference in potential as measured from the bottom of the conduction band to  $E_f$ ). For good conductors such as metals,  $E_f$  is a positive quantity and usually decreases in absolute value with a rise in temperature, but it can also increase, as will be shown later.

It has long been assumed that the temperature coefficient of the work function,  $\alpha$ , for metals has a positive value of the order of  $10^{-4}$  -  $10^{-5}$  ev/deg. However, it should be pointed out that most of the experimental work that was done in determining these values occurred prior to 1940. A tabulation of these results is given in Table 1. The problems involved in obtaining pure materials, clean surfaces, and a high vacuum were considerable in those days, and therefore many of these results should probably be questioned. Several recent experimental investigations, including studies of single crystal surfaces, under carefully controlled conditions has indicated that this is the case. Values for  $\alpha$  appear to be as high as  $10^{-2}$  -  $10^{-3}$  ev/deg and in fact may be negative or positive.

Some of the important factors that appear to affect  $\alpha$  are the coefficient of thermal expansion, the internal electrostatic effect of atomic vibrations, and the electron affinity (at the surface, an important component of the electron affinity is the double dipole layer). These factors are discussed below:

1. Fermi level — The Fermi level,  $E_f$ , of a conductor can be obtained from the use of Fermi-Dirac statistics and can be defined as that energy at which the probability of a quantum energy state being filled is just one-half. Quantitative values of  $E_f$  are obtained from the requirement that no matter how they are distributed the number of electrons in the conductor must be a known value. The first step is, therefore, to add up all the electrons in the possible energy states and equate them to the known number of electrons  $N$ . This gives:

**TABLE 1**  
**TEMPERATURE COEFFICIENT OF THE WORK**  
**FUNCTION OF SOME METALS**

Material	Temperature Range (°K)	$\alpha$ 1v/°K	Reference
Be	80-300	$1 \times 10^{-4}$	1
Bi	80-300	$1 \times 10^{-4}$	1
Mo	300-900	$6 \times 10^{-5}$	2
Pd	300-1100	$1.3 \times 10^{-5}$	2
Ta	300-1000	$7 \times 10^{-5}$	3
"	300-1000	$7 \times 10^{-5}$	4
"	2000-2600	$6 \times 10^{-5}$	5
W	2100-2700	$6 \times 10^{-5}$	5
"	300-950	$6 \times 10^{-5}$	6
"	300-1100	$6 \times 10^{-5}$	7
"	300-950	$6.3 \times 10^{-5}$	8

$$\int_0^{\infty} \frac{D(E) dE}{1 + e^{\frac{E - E_f}{kT}}} \quad (1)$$

where  $D(E)$  is the density of states function. The final evaluation of  $E_f$  at  $T = 0^\circ\text{K}$  is shown as:

$$E_f = \frac{h^2}{2m} \left( \frac{3N}{4\pi G} \right)^{2/3} - \frac{\pi^2}{12} \frac{2m (kT)^2}{h^2} \left( \frac{4\pi G}{3N} \right)^{2/3} + \dots \quad (2)$$

At  $T = 0^\circ\text{K}$ ,  $E_f = E_{f0}$ . Then:

$$E_{f0} = \frac{h^2}{2m} \left( \frac{3N}{4\pi G} \right)^{2/3} \quad (3)$$

thus

$$E_f = E_{f0} \left[ 1 - \frac{\pi^2}{12} \left( \frac{kT}{E_{f0}} \right)^2 \right] \quad (4)$$

where  $N$  = the total number of free electrons per unit volume and is very roughly estimated from the number of free electrons per atom,  $n$ , Avogadro's number,  $L$ , the density,  $\delta$ , and the atomic weight of the metal,  $A_w$ . Thus

$$N = n \frac{\delta}{A_w} L \text{ cm}^{-3}$$

$G$  = occupancy number (depends on the azimuthal quantum number); equals 2 for an  $s$  state

$m, k$ , and  $h$  have been previously defined.

Using the definition of  $N$  as given above and Equation (2)  $E_{f0}$  can be approximated as:

$$E_{f0} = 26.1 \left( \frac{\delta n}{A_w} \right)^{2/3} \text{ ev.} \quad (5)$$

A table is given below showing calculated values of  $E_{f0} n^{-2/3}$  (it should be realized that although  $n$  is estimated to be one free electron per atom its actual value is unknown).

TABLE 2  
LIMITING ENERGY OF SOME METALS

$E_{f0} n^{-2/3}$ ev.	$E_{f0} n^{-2/3}$ ev.	$E_{f0} n^{-2/3}$ ev.
Li 4.7	Be 9.0	Th 3.5
Na 3.2	Mg 4.5	Ta 5.3
K 2.1	Ca 3.0	Mo 5.8
Rb 1.8	Sr 2.5	W 5.8
Cs 1.5	Ba 2.4	Fe 7.1
Cu 7.0	Al 5.6	Ni 7.4
Ag 5.5		Pd 6.1
Au 5.5		Pt 6.0

Since  $E_{f0}$  is usually greater than 2 ev. for metals and  $kT$  is only .12 ev at  $1500^{\circ}\text{K}$ , it can be seen from Equation (3) that the shift of Fermi level with temperature appears to be very small. For example, at  $2000^{\circ}\text{K}$  the shift of the Fermi level for tungsten is approximately 0.004 ev. and can be neglected for practical purposes. However, it was felt that an introductory calculation would be desirable, since in semiconductors the change of the Fermi level with temperature may be substantial and frequently a mistaken opinion is that the analogous change in the Fermi level for metals will account for most of the change in work function.

2. Coefficient of thermal expansion — This parameter appears to have received more attention by theoreticians than any other one. Quantum-mechanical calculations of the magnitude of this effect have been made by Herzfeld (9), Blochinzev and Drabkina (10), Reimann (11), Seely (12) and Wigner (13). Use was made of such entities as the Fermi-Thomas model, the Sommerfield free electron model, the Slater-Flock self-consistent field equations, and Wigner and Bardeen's expression for the work function and its relationship to the Coulomb energy, and the correlation and exchange energies for an electron moving in the field of the ion cores of a metal (14).

For many metals a simplified approximation of the effect of thermal expansion on the temperature coefficient of the work function may be obtained

from the use of Equations (2) and (3), and the temperature dependence of  $N$  (defined above) due to the increase of volume with increasing temperature. The correction factor in Equation (4) can be dismissed as being negligible. If a linear coefficient of thermal expansion,  $\beta$ , is assumed, and the volume at a finite temperature,  $V_1 = V_0 (1 + \beta T)^3$ , the following equations are obtained:

$$E_{f^0} = \frac{h^2}{2m} \left( \frac{3 nL}{4 \pi G V_0} \right)^{2/3} \quad (6)$$

(This is actually Equation (3) with  $N = \frac{nL}{V_0}$  ).

$$E_f = \frac{h^2}{2m} \left( \frac{3 nL}{4 \pi G V_0 (1 + \beta T)^3} \right)^{2/3} \quad (7)$$

or

$$E_f = E_{f^0} \left[ \frac{1}{(1 + \beta T)^2} \right] = E_{f^0} (1 - 2\beta T) \quad (8)$$

A representative calculation (using Equation (8)) for polycrystalline tungsten at 2000°K is shown as:

$$\begin{aligned} E_f &= E_{f^0} \left[ 1 - (2.6 \times 10^{-6} \cdot 2000) \right] \text{ ev.} \\ &= 5.66 \text{ ev.} \end{aligned}$$

Thus, the thermal expansion coefficient of the Fermi level,  $\alpha_1$ , would be

$$\frac{E_f - E_{f^0}}{T} = - \frac{.140}{2000} = - 7 \times 10^{-5} \text{ ev/deg.}$$

Since a lowering of the Fermi level results in an increase in the work function,  $\phi$ , the thermal expansion contribution as calculated above would show a positive effect on  $\phi$ . If the experimental value of,  $\alpha$ , for polycrystalline tungsten that has been most frequently published in the literature is taken to be  $6 \times 10^{-5}$  ev/deg. it can be seen that  $\alpha$  and  $\alpha_1$  are quite close to each other in

magnitude and at least indicates that the thermal expansion characteristics of a solid may have an important effect on  $\alpha$ . Equation (8) as used in the previous example is probably not correct for all metals since Sun Nien Tai (15) and Wohlfahrt (16) have considered that the temperature dependence of the Fermi level will be different from that shown by Equation (8) if the highest energy bands overlap or if the Fermi level is very close to the top or bottom of the respective bands. The difference then obtained is due to the transfer of electrons from one band to the other with rising temperature. Actually, in the case of nickel a positive temperature dependence of  $E_f$  instead of the negative one given by Equation (8) has been calculated.

3. Electron affinity — The most likely factors contributing to the temperature variation of the total potential barrier of a conductor is, once again, thermal expansion effects. However, the effect of this phenomenon on the temperature coefficient of the work function appears to be quite small. The particular parameter that is affected is the magnitude of the surface dipole layer,  $D$  which, as discussed in the first summary report of this contract, (14) is formed on a hypothetical clean surface of a solid according to the quantum-mechanical considerations of Bardeen and Wigner (17). If these quantum-mechanical calculations were to be made for different values of the lattice constant, appreciably different results for  $D$  would be obtained. Herring and Nichols (18) made a crude estimate of the magnitude of this effect by noting that if the atoms of a metal could be squeezed together or pulled apart at will, a plot of  $D$  against lattice constant ought to resemble the following plot

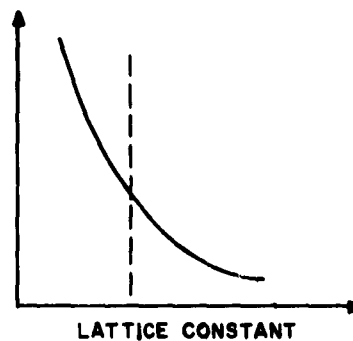


Figure 1 - Schematic Variation of Double Layer Moment  $D$  with Lattice Constant

1

Taking  $D$  to be of the order of one to several volts for a metal such as tungsten, a negative temperature coefficient for  $D$  of the order of perhaps one half that of Boltzmann's constant,  $k$ , was obtained. This, of course, would tend to lower the total work function of the metal. Other effects such as the roughening of the surface by thermal vibrations or the increase in the extension of the electron cloud outside the surface due to the thermal energies of the electrons, probably have a much smaller effect on the temperature coefficient of  $D$  than thermal expansion.

4. In addition to the above theoretical considerations, it should be realized, however, that many thermionic emission experiments have been carried out under inadequate vacuum conditions, thereby contributing a temperature dependent contamination of the surface by adsorbed gas atoms. Since the number of adsorbed atoms depend strongly upon the temperature of the solid surface, the change in the electron affinity may be greatest at low temperatures, and decrease at higher temperatures. This change, of course, can be either positive or negative depending upon whether the adsorbed atoms are electronegative or electropositive.

Another factor which should also be taken into consideration is that polycrystalline surfaces, after being heat treated in a high vacuum will, generally exhibit different crystal facets (crystallographic planes) for the individual crystals that make up the surface. Since these facets are likely to have different work functions the amount of adsorbed atoms on a surface can be quite different when adsorbed on high index planes versus those with low indices. This will be discussed in greater detail in Section 4 of this report. On a polycrystalline surface, in addition to the quantum-mechanical considerations previously discussed local contact differences in potential fields between facets will make the specification of a suitable choice for the electron affinity quite difficult. The expression "patch effect" is used to describe this condition qualitatively.

The results of experimental determinations of the work function of selective crystallographic planes of metallic single crystals have been published by only a few investigators to date (19, 20, 21, 22, 23). The substance that has been investigated most (until quite recently) has been tungsten and it is now concluded that planes with various miller indices ( $h, k, l$ )

can have considerably different values for work functions. Thus, while the average value for polycrystalline tungsten is generally agreed to be  $\sim 4.56$  ev., the actual work function for planes such as the 114 may be 4.2 ev., (25),  $\phi = 4.30$  ev. for the 111 plane, (25),  $\phi = 4.71$  for the 100 plane, (23), and for the 110 plane  $\phi$  may be as high as 5.5-6.0 ev. (23). Several new tools which have done most to show differences due to various crystal planes are the field and ion emission microscope (and the ion gauge, used to measure rapid changes in pressure during adsorption and flash-off). The highest electron emissions are seen to come from the higher index planes which are more densely packed with atoms than the lower index planes. Another contributing factor to the difference in work function may also come about from the fact that tungsten surface atoms may have four, five or six nearest neighbors whereas in the interior of a crystal, each tungsten atom touches 8 nearest neighbors. The tungsten atoms with fewer neighbors will have more electrons available for thermionic emission. In any case it is apparently the change in the magnitude of the dipole moment per unit area at the surface of the various planes which is being affected. Some of the considerations pertaining to the effect of different lattice constants on this dipole moment have been previously reviewed. Smoluchowski (24) who made use of the Fermi-Thomas statistical model theorized that in crystallographic planes where the atoms are far enough apart, the surface is considered to be "rough" due to the tendency of the electron charge distribution to show high peaks and deep valleys. This led to a postulation that a gradual "smoothing out" process of this charge distribution occurs, and therefore, it is this phenomena which makes the difference in work function as higher index planes are considered. However, it is felt that the exact prediction of the order of the faces of decreasing dipole moment is still beyond present-day theory, even for the simplest metals.

Hutson (25) appears to have published the only data pertaining to the temperature dependency of the work function for various planes of tungsten, this is shown below:



**TABLE 3**  
**TEMPERATURE COEFFICIENT OF THE WORK FUNCTION OF SOME**  
**CRYSTALLOGRAPHIC PLANES OF TUNGSTEN**

Orientation	(ev/deg)
111	+ 3 x 10 <sup>-5</sup>
112	- 5 to 8 x 10 <sup>-5</sup>
116	+ 3 x 10 <sup>-5</sup>
100	- 2 x 10 <sup>-5</sup>

Thus, it is seen that the possibility arises that negative coefficients of  $\alpha$ , as well as positive values may occur, depending on which planes of a crystal are being considered.

Another investigation which is of great importance to this study has been Blevins and Crowell's (27) recent determination of the temperature dependence of the work functions of single crystal surfaces of copper. Measurements of  $\alpha$  for the 100, 111, 211, and 221 crystal faces were taken from 300°K to 900°K and indicated values ranging from  $-3.4 \times 10^{-3}$  in the 111 direction to  $-4.2 \times 10^{-2}$  ev/°K in the 110 direction. These latter values are at least two orders of magnitude greater than those obtained previously for metals. The effect of individual crystallographic planes is shown to play a major role in the theoretical interpretation of  $\alpha$ .

Recently Crowell and Armstrong (26), following Herring and Nichols' semiquantitative theory of the temperature dependence of the work function, have divided the work function into two terms; one due to thermal expansion and the other due to the electrostatic effect of thermal vibrations at constant volume:

$$\frac{d\phi}{dT} = 3\beta V \left( \frac{\partial \phi}{\partial V} \right)_T + \left( \frac{\partial \phi}{\partial T} \right)_V \quad (9)$$

Utilizing various quantum-mechanical derivations, calculations were made of  $\frac{d\phi}{dT}$  for several monovalent metals from the alkali's and the group IB. They compared these calculations with the results of experimental work using a contact potential type of measurement and found surprisingly good correlation between their theory and experiment. This is shown in the following table.

TABLE 4  
COMPARISON OF THEORY AND EXPERIMENT

Element	$d\phi/dT$ (EXPT.) $10^{-5}$ ev/ $^{\circ}$ K	$d\phi/dT$ (Theory) $10^{-5}$ ev/ $^{\circ}$ K
Ag	-13.4	-11.8
Cu	(-6)	-14.3
Na	-51	-45
K	-26	-28

The largest contribution to the temperature dependence of the work function is attributed to the second half of Equation (9) and is a negative value even though it is reduced by the positive coefficient of the thermal expansion effect. In relating this work to our previous discussion it should be noted that for three out of four of the metals listed in Table 4 the calculated value for the Fermi level (Table 1) gives a location either close to the bottom or top of the conduction band since the total width of the conduction band for most metals is approximately 10 ev.

In summing up this study of the factors which may have a bearing on the magnitude of  $\alpha$ , it has been shown that experimentally the work function of a metal can increase or decrease with the temperature depending on the relative rates of change of such parameters as the Fermi level, electron affinity, and the internal electrostatic potential. Though, the final solution to the problem is still in doubt, the continuous progress that is being made in understanding what is happening at the surface of solids should provide some needed answers.

In the above discussion we have to a large extent been concerned with the true work function of a solid; which is primarily a theoretical concept to be used in discussions involving a theoretical model of the surface. While its evaluation is frequently the goal of experimental measurements, the information obtained from these experiments discussed above is usually insufficient for its unique determination. Theoretically, the effective work function of a metal  $\phi_e$ , which is obtained by direct substitution of the temperature and emission current density into the Richardson-Dushman equation approximates the true work function if the Richardson "A" is taken to be  $120 \text{ amps/cm}^2/\text{°K}$  and the reflection coefficient at the surface to be zero. The Richardson work function,  $\phi_r$ , may be obtained from an extrapolation of the plot of the effective work function,  $\phi_e$ , versus temperature to  $0^\circ\text{K}$ .  $\phi_r$  is thus equal to  $\phi_e - \alpha_e T$ , where  $\alpha_e$  is the temperature coefficient of the effective work function. The Richardson constant, A, may be obtained from the temperature dependence of the effective work function and will be equal to  $120 \text{ amps/cm}^2/\text{°K}$  when the temperature dependence of the effective work function is equal to zero. This will be discussed in more detail in Section 3. In considering the effective work function as being close to the true work function of a solid, the difficulty of analyzing the effects of such factors as the reflection coefficient, the patch effect, and the uncertainty of the effective emitting area must be taken into consideration. For this reason, in the case of metals, the Richardson slope method of determining work function may well give the best value of  $\phi$  that can be obtained from direct thermionic emission measurements.

### 3. Temperature Coefficient of the Work Function for Semiconductors

#### a. Temperature Coefficient of the Fermi Level

The principal factor contributing to theoretical calculations of the temperature dependence of the true work function for semiconductors appears to be the temperature dependence of the Fermi level. A review of semiconductor theory has shown that the location of the Fermi level is largely dependent upon the following parameters which pertain to semiconductors in general.

$E_f$	=	location of the Fermi level
$E_c$	=	location of bottom of conduction band
$E_v$	=	location of top of valence band
$E_g$	=	width of the band gap in ev.
$N_d$	=	number of donors $\text{cm}^{-3}$
$N_a$	=	number of acceptors $\text{cm}^{-3}$
$m_n, m_p$	=	effective mass of electrons and holes in the conduction band and valence band.
$N_c$	=	density of states in the conduction band = $2 (2\pi m_n kT/h^2)^{3/2}$ = $4.82 \cdot 10^{15}$
$n$	=	density of excess electrons in the conduction band = $N_c e^{-(E_c - E_f)/kT}$
$E_d$	=	location of major donor impurity level relative to the bottom of the conduction band
$E_a$	=	location of major acceptor level relative to the donor level and the top of the valence band
$n_d$	=	density of excess electrons bound to donors
$n_p$	=	density of holes bound to acceptors
$p$	=	density of holes in the conduction band $N_v e^{-(E_f - E_v)/kT}$
$N_v$	=	effective density of states in valence band = $2(2\pi m_p kT/h^2)^{3/2}$

The application of Fermi-Dirac statistics is frequently utilized in describing the interior of a semiconductor. Values for most of the above defined

factors are thus seen to be mainly determined by the distribution of quantum energy states, the Fermi level, and the temperature. The essential condition to be remembered in describing a semiconductor is the necessity for maintaining electrical neutrality in the material. In other words, the sum of the positive charges must equal the sum of the negative charges; in a semiconductor with donors and acceptors the following equation describes this equilibrium condition.

$$e(N_d - N_a) - e(n + n_d - p) = 0 \quad (1)$$

or

$$n + n_d + N_a = p + n_p + N_d$$

The requirement of electrical neutrality is used in applying a graphical type of solution to the difficult problem of determining the value of the Fermi level for a given semiconductor model at a specified temperature. Given various quantities such as  $E_v$ ,  $E_a$ ,  $E_c$ ,  $m_n$ ,  $m_p$ , together with the donor and acceptor concentrations, and using the various assumptions and equations defining and relating these terms, it is then possible to plot the left and right sides of Equation (1) each as a function of  $E_f$ . Examples of this type of graphical analysis are given in Shockley's well known treatise on semiconductor theory (28). In Figures 2 and 3 each component of Equation (1) is plotted on a logarithmic scale as a function of  $E_f$  for  $T = 300^\circ\text{K}$ , and  $600^\circ\text{F}$  respectively. The middle of the band gap is taken to be zero. Positive charges are drawn as solid lines and their sum, which is the right side of Equation (1) is shown by a heavy line. The density of negative charges are similarly indicated by dashed lines. Where the heavy lines cross, Equation (1) is satisfied; the conditions for electrical neutrality are realized, and the exact value of  $E_f$  is obtained. In looking at these plots it should be realized that electrical behavior in semiconductors depend to a large extent in which of the three temperature regions measurements are made. These regions are identified as the bound, saturation, or intrinsic region and are shown in Figure 4.

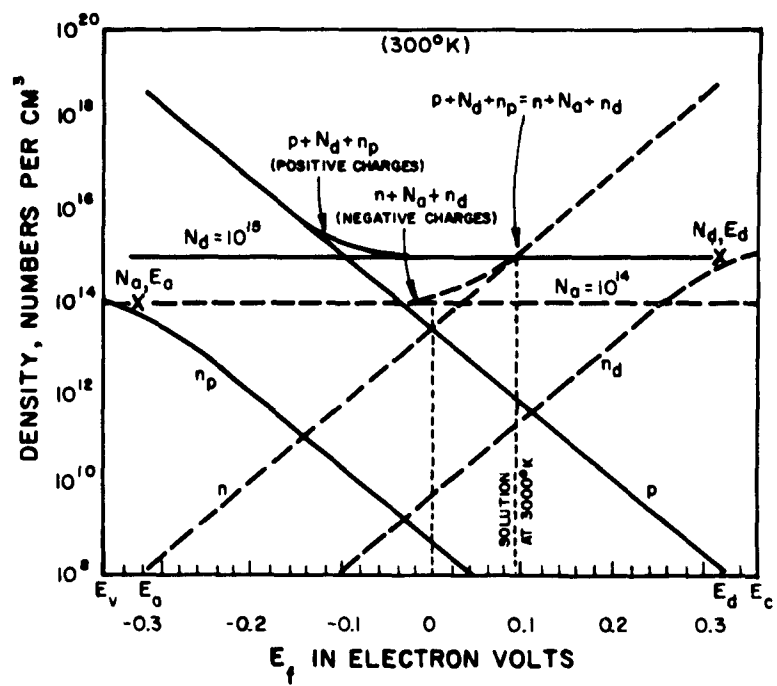


Figure 2 - Solution for  $E_f$  with  $N_a = 10^{14} \text{ cm}^{-2}$   
 $m_n = 0.25 m$ ,  $m_p = 0.3 m$ ,  $N_d = 10^{15} \text{ cm}^{-3}$   
 and  $T \approx 300^\circ\text{K}$

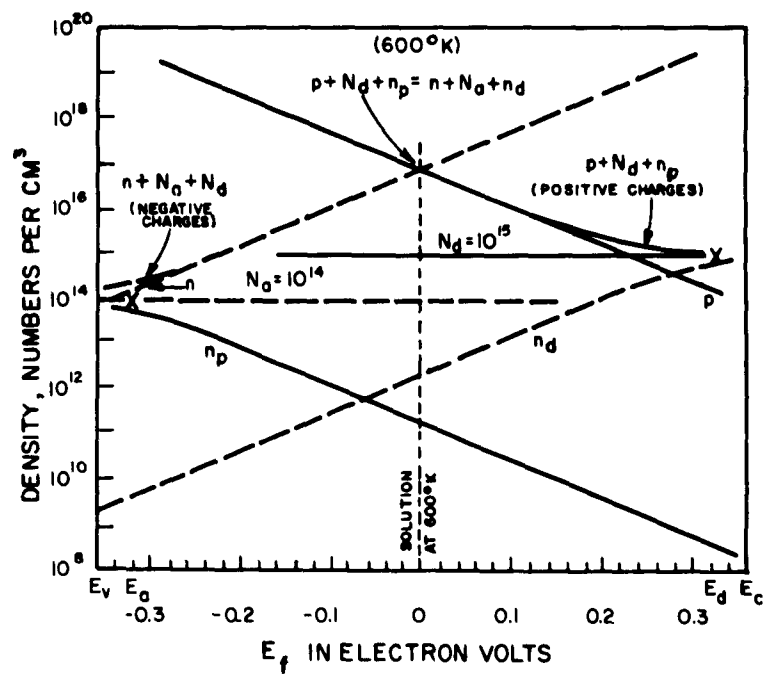


Figure 3 - Solution for  $E_f$ ,  $N_a = 10^{14} \text{ cm}^{-3}$ ,  $m_n = 0.25 m$ ,  $m_p = 0.3 m$ ,  $N_d = 10^{15} \text{ cm}^{-3}$  and  $T \approx 600^\circ\text{K}$

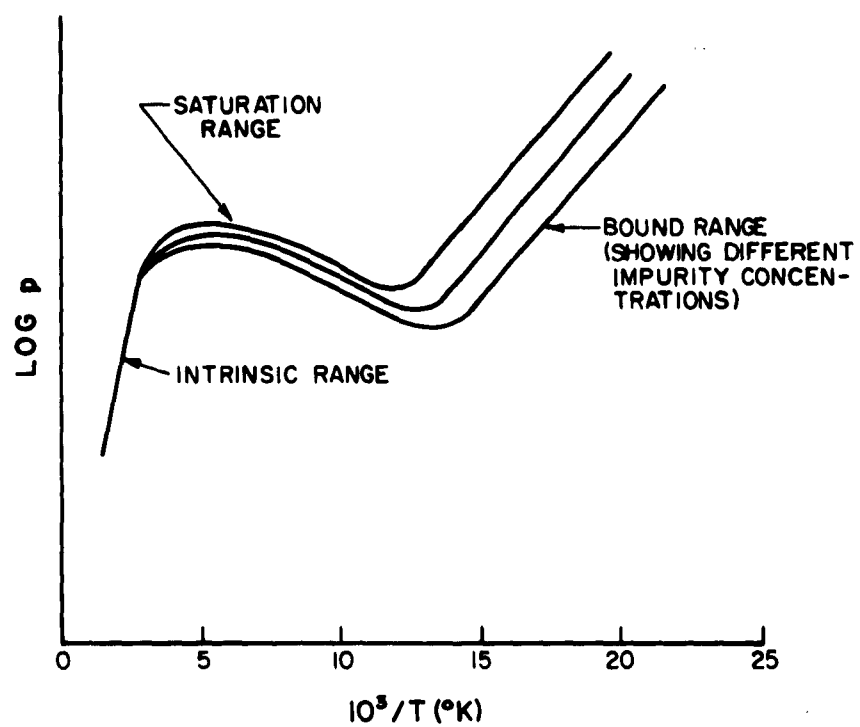


Figure 4 -  $\log$  Resistivity vs.  $1/T^{\circ}$



The upper set of curves in Figure 4 refers to a typical semiconductor whose conduction is due mainly to impurity excitation. If  $N_a$  were equal to zero, the Fermi level at  $0^\circ\text{K}$  would be located half way between  $E_c$  and  $E_d$ ; however, this situation is impossible, practically (some acceptors are always present in the solid), and  $E_f$  is always located closer to the donor level than anticipated. Depending on the concentration of acceptors, the Fermi level may rise or fall initially (See Figure 4) with an increase in temperature, but eventually it will always fall.

In the example given by Shockley (Figure 5) the Fermi level rises from  $0^\circ\text{K}$  to  $10^\circ\text{K}$  before it reaches a maximum value, because although electrons are being excited to the conduction band,  $n + n_d$  must be kept constant. The saturation range is entered as soon as  $E_f$  has fallen a few  $kT$  below  $E_d$  so that the donor levels are substantially empty and the equation  $n = N_d - N_a$  holds. In the saturation region a drop in conductivity with rising temperature occurs because although the carrier concentration is constant the mobility of the carriers decreases with rising temperature due to various factors attributed mostly to lattice scattering. Finally, at temperatures greater than  $400^\circ\text{C}$ ,  $E_f$  is down to a position located within a few  $kT$  above the midpoint between the bands; the intrinsic region is now reached, whereupon appreciable numbers of electrons begin to be excited across the band gap creating at the same time an appreciable number of holes. At still higher temperatures  $E_f$  approaches the midpoint even more closely, for otherwise either the holes or the electrons would greatly outnumber the other and the rule of electrical neutrality requires that  $E_f = (E_v + E_c)/2$ , if  $p = n$ . In the intrinsic region a very steep rise in the conductivity occurs, which is shown in a  $\log \rho$  vs  $\frac{1}{T}$  plot (Figure 4). This state of intrinsic conduction will be reached in every semiconductor at a sufficiently high temperature, provided that the solid does not melt or vaporize appreciably.

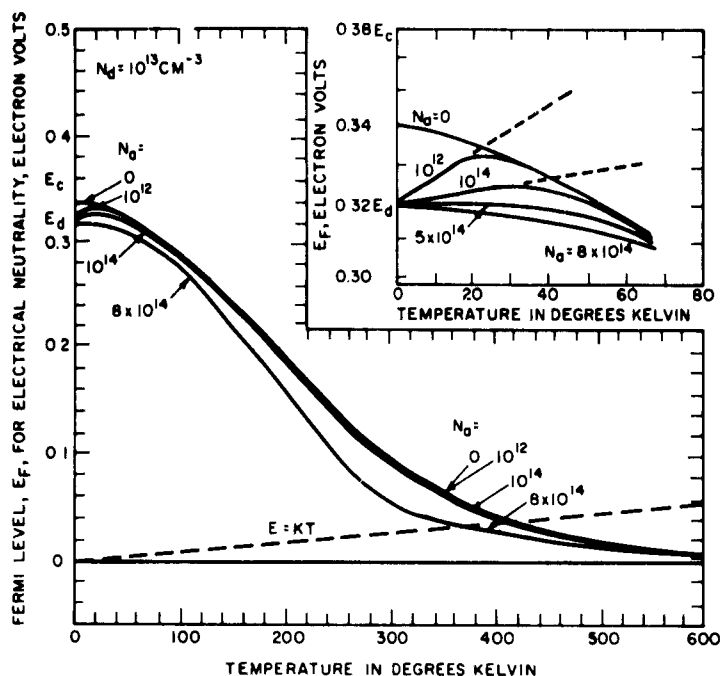


Figure 5 - The Fermi Level for Electrical Neutrality Plotted Against Temperature for Several Densities of Acceptors

A study of the above example indicates that when the donor and acceptor densities in a semiconductor happen to be of comparable magnitude the behavior of the temperature coefficient of the Fermi level becomes more difficult to describe.

The discussion so far has been concerned with an n-type semiconductor. If a p-type semiconductor (containing an excess of acceptors over donors) is considered, then a similar behavior of the Fermi level will occur except that the Fermi level will always rise when the temperature is raised. As the temperature increases, a limiting value will eventually be reached for the Fermi level. This limiting value for both n and p type semiconductors closely approaches the midpoint of the band gap, which by itself may apparently have a negative temperature coefficient of the order of  $10^{-4}$  ev. /  $^{\circ}\text{K}$ . This phenomenon will be discussed later.

#### b. Approximations - Fowler Equation

Because of the fact that exact calculations of the Fermi energy for a complex semiconductor may be a very difficult task, approximations to the solution of the problem have been applied to particular semiconductor models (29, 30, 31, 32). The first and most important of these approximations

applies to semiconductors containing a single donor level which is largely filled up with electrons. The effect of the valence band and the acceptor levels are neglected. Once again the rule of electrical neutrality,  $n + n_d = N_d$  is followed, where  $n = N_c e^{-E_f/kT}$  (it is permissible to consider  $E_c$  as the zero energy level, with  $E_f$  being measured positively down from the conduction band) and  $n_d = fN_d$ ;  $f$  is defined as the Fermi factor,  $f = \frac{1}{1 + \exp[-(E_d - E_f)/kT]}$  and is the probability of having the donor level,  $E_d$ , occupied by an electron (28). It then follows that:

$$n_d = \frac{N_d}{1 + \exp[-(E_d - E_f)/kT]} \quad (2)$$

Upon substituting the above definitions of  $n$  and  $n_d$  into the neutrality equation it is seen that

$$N_c e^{-E_f/kT} \approx N_d \left[ \frac{e^{-E_d - E_c/kT}}{e^{-E_d - E_f/kT} + 1} \right] \quad (3)$$

If  $E_f \leq E_d - 4kT$ , then a further simplification,

$$n_c e^{-E_f/kT} \approx N_d e^{\frac{E_f - E_d}{kT}} \quad (4)$$

is possible, from which

$$E_f = E_{fo} + \frac{kT}{2} \ln \frac{N_c}{N_d} \quad (5)$$

If Equation (5) is then substituted into the Richardson-Dushman equation, which may be written as  $J = AT^2 \exp - \left[ \frac{\chi + E_f}{kT} \right]$ , where  $\chi$  is the electron affinity, then

$$J = A' N_d^{1/2} T^{5/4} \exp - (\phi_o/kT) \quad (6)$$

where  $A' = 1.730 \times 10^{-6}$  amps/cm<sup>1/2</sup> deg<sup>5/4</sup> and  $\phi_o = \chi + E_{fo}$ .

This equation is the well known Fowler equation for the thermionic emission of semiconductors. If a Richardson type plot of  $\log J/T^{5/4}$  vs  $1/T$  is made, the slope will give  $\phi_0$  and the intercept at  $1/T$  will then determine  $N_d$  as well as the temperature dependence of the work function. Once again it must be emphasized that this equation comes from an idealized model of a semiconductor, and that the presence of a sufficient number of acceptors and the location of their energy level may modify the above situation substantially. The Fowler equation also becomes more approximate with an increase in temperature which results in the continuous drop of the Fermi level, as the saturation region is approached. The lower the concentration of donors, the more rapid the effect of the rising temperature on the approximations that are used with the Fowler equation. Certainly a knowledge of the approximate location of the Fermi level, especially with regards to the donor level, helps considerably when using the Richardson-Dushman or Fowler equation in interpreting the thermionic emission from semiconductors.

If the saturation region for a semiconductor is closely approached or  $E_f$  is approximately  $\geq E_d + 4kT$ , another approximation for calculating the Fermi level can be used. Equation (3) becomes

$$n = N_c \exp - (E_f/kT) \approx N_d \quad (7)$$

which leads to

$$E_f = kT \ln \frac{N_c}{N_d} \quad (8)$$

Upon substituting Equation (8) into the Richardson-Dushman equation it is seen that

$$J = A'' T^{1/2} N_d \exp - (\chi/kT) \quad (9)$$

where  $A'' = 2.488 \times 10^{-14}$  amps-cm/ $^{\circ}K^{1/2}$ .

In this case the slope of a  $\log J/T^{1/2}$  vs  $1/T$  plot yields  $\chi$ , and  $N_d$  may be evaluated from the intercept. Thus, in evaluating semiconductors, it is probable that if conductivity measurements show temperature-independent behavior (the saturation region is thus assumed), Equation (9) is more likely to hold for thermionic emission than the usual Richardson or Fowler equation. In addition to the two approximations described above there are two analogous approximations which apply for p-type semiconductors.

One additional approximation should be mentioned; that is the one dealing with intrinsic conduction of semiconductors. In this case, of course, the Fermi level will be located very close to the middle of the band gap, and will be dependent upon the following:

$$E_f = \frac{E_g}{2} + \frac{3}{4} kT \ln \frac{m_p}{m_n} \quad (10)$$

It should be pointed out, however, that no semiconductors that have been operated at the usual thermionic temperatures are known to be in the intrinsic region.

### c. Possible Mechanism of Oxide Coated Cathode

Many attempts have been made in the past to interpret the mechanisms of conduction and thermionic emission of (Ba-Sr)O cathodes in various stages of activation. One particular approach, has followed the original classical concepts of Wilson (29) and Fowler (30) in which both Maxwell-Boltzmann and Fermi statistics were applied and both donors and acceptors are considered. DuPré and his co-workers (33) utilized the following equations:

$$\begin{aligned} 2(2\pi m_n kT/h^2)^{3/2} e^{E_f/kT} &= N_d / 1 + e^{-(E_f - E_d)/kT} \\ &- N_a / 1 + e^{-(E_f - E_a)/kT} \\ &+ 2 \left[ 2\pi m_p kT/h^2 \right]^{3/2} e^{-(E_f - E_g)/kT} \end{aligned} \quad (11)$$

( $E_c$  is zero, and  $E_f$  is measured negatively downward from the conduction band). In using the above equation the requirement of electrical neutrality is again maintained, with the number of positive charges equaling the number of negative charges as shown by

$$p + n_d^+ = n + n_p^- \quad (12)$$

where  $p$  and  $n$  are previously defined, and  $n_d^+$  and  $n_p^-$  are the concentration of ionized donors and acceptors respectively.

Their proposed semiconductor model consisted of a band gap of 1.7 ev., a major donor level 0.3 ev. below the conduction band, an acceptor level 1 ev. below the conduction band, and an electron affinity of 1 ev. It was assumed for simplicity that a constant density of acceptors existed ( $1.5 \times 10^{17}/\text{cm}^3$ ) and the process of activation was interpreted as a gradual increase of the donors, which are thought to arise from the formation of excess barium. The presence of acceptors are attributed to such factors as impurities, surface states, and lattice defects. A chemical analysis of a well activated cathode gave an excess barium concentration of  $3 \times 10^{17}/\text{cm}^3$  and estimated various concentrations for partially deactivated stages were given as 1.6, 1.5 and  $1 \times 10^{17}$  donors/ $\text{cm}^3$ . Plots were made of the calculated variation of the Fermi level with temperatures (See Figure 6) which allowed the determination of the true work function,  $\phi_t$ , for the various donor concentrations, since according to theory  $\phi_t = \chi + E_f$  for a semiconductor, where  $E_f$  is the temperature dependent value of the Fermi level and is measured downward from the bottom of the conduction band, and  $\chi$  is the electron affinity. In the temperature range from  $\sim 800^\circ\text{K}$  to  $1100^\circ\text{K}$ ,  $E_f$  for the n-type semiconductor can be approximated by a straight line and can be represented by the formula

$$E_f = E_{f0} + \alpha T, \quad (13)$$

where  $E_{f0}$  is the result of the extrapolation of the straight line to  $T = 0^\circ\text{K}$ , and  $\alpha$  is the temperature dependence of the Fermi level. If  $\chi$ ,  $E_{f0}$  and  $\alpha$

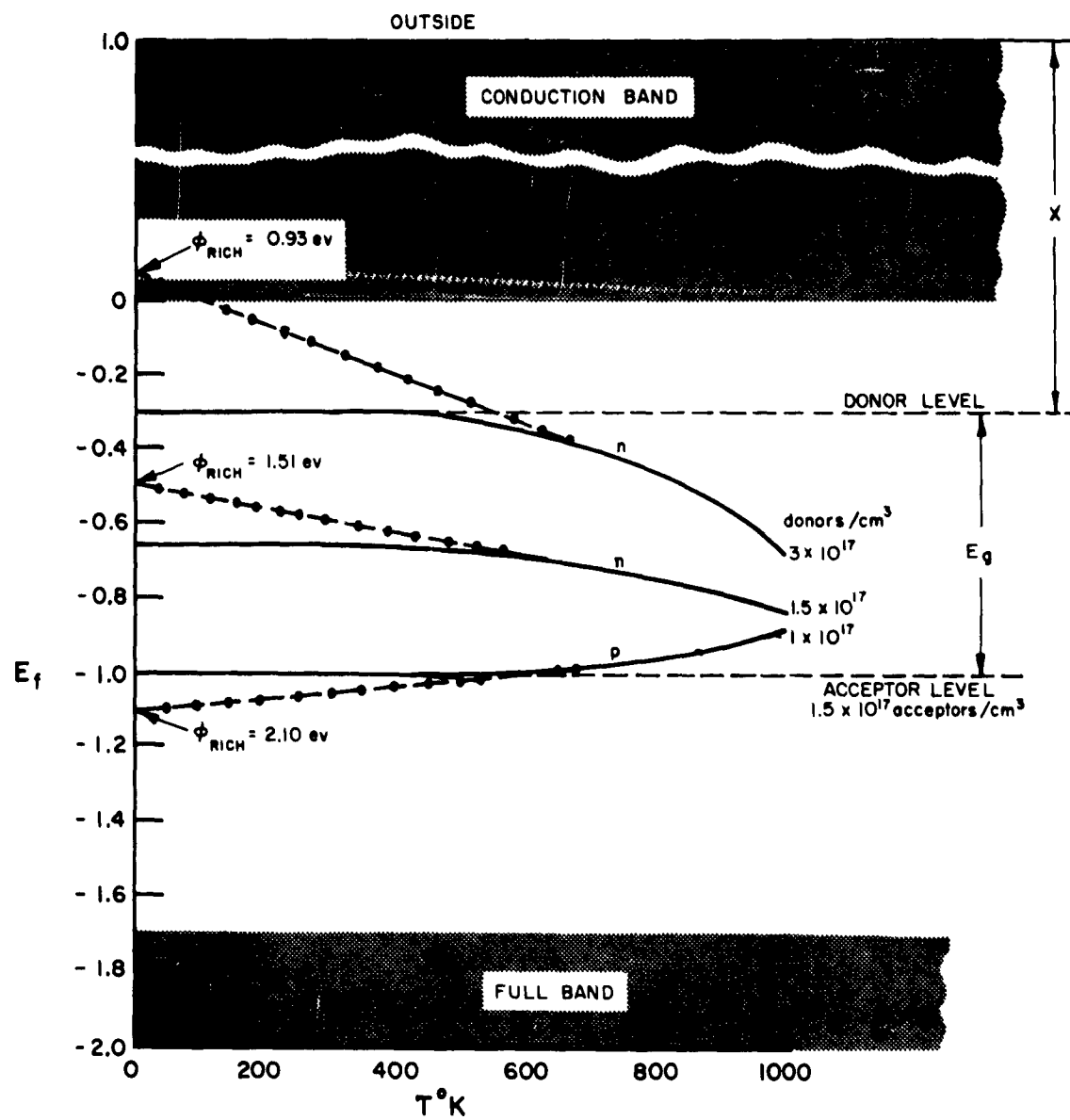


Figure 6 - Variation of Fermi Level,  $E_f$  with Temperature for Three Donor Concentrations

are now substituted into the Richardson-Dushman equation, the following is obtained:

$$J = AT^2 \exp - (\chi + E_f o + \alpha T)/kT = AT^2 e^{-\alpha/k} e^{-(\chi + E_f o)/kT} \quad (14)$$

where  $\chi + E_f o$  is the Richardson work function as usually defined and is theoretically equal to the Rich  $\phi$  which is shown in Figure 6. In a normal Richardson plot where  $\log J/T^2$  is plotted against  $\frac{1}{T}$ , the intercept at  $1/T = 0$  should give the value  $A' = 120 e^{-\alpha/kT}$  with the slope yielding  $\chi + E_f o$ , or  $\phi_o$ . However, the true work function is  $\chi + E_f o + \alpha T$  and if a high enough value of  $\alpha$  occurs can be considerably different from the Rich  $\phi$ . It must also be pointed out that the example given in Figure 6, the Richardson-Dushman equation would only be applicable in the region  $> 800^\circ K$  while for lower temperatures an interpretation of the true thermionic emission would become more difficult, and theoretical calculations using classical statistics may have to be made for the exact location of the Fermi level, provided that a reasonable knowledge of  $E_d$ ,  $E_a$ ,  $E_g$ ,  $N_d$ , etc. is obtained. In the case of a p-type semiconductor it should be realized that the Fermi level would rise with temperature and therefore  $\alpha$  would be negative and  $A > 120 \text{ amps/cm}^2 \text{ deg}^2$ . It should be pointed out that the plots in Figure 6 represent approximate data in the bound region only, since the saturation region apparently is never reached in the usual (Ba, Sr)O cathodes, which are considered here. In any case, the above discussion appears to indicate that the most accurate value for the thermionic work function in semiconductors can usually be obtained either from the absolute value of the emission current in the theoretical Richardson equation (or by the use of the Kelvin type of contact potential measurement). However, a word of caution should be injected into this interpretation since other important factors have not been taken into account, such as the influence of surface states, surface inhomogeneity (patch effect), the temperature dependence of the electron affinity, and the temperature dependence of the band gap.

Bardeen (34) postulated the existence of surface states to explain certain experimental results which show the relative insensitivity of the work function of semiconductors such as germanium and silicon to temperature or widely different donor concentrations. He considered that surface states create a space charge or dipole-layer region (the thickness of the dipole layer is determined by the distribution of energy levels in the band gap at the surface) in the



vicinity of a semiconductor surface, which cause the conduction and valence bands to curve either upward or downward at the surface thus nullifying to a large extent the shift that may occur in the bulk Fermi level. In other words, the Fermi level may be "locked" to the top of the surface barrier. Surface states are considered to be associated with dangling bonds caused by the interruption of the crystalline structure at the surface (Tamm levels), impurities adsorbed on the surface, and imperfections existing either on the uncontaminated or the contaminated surface. Investigations of the surface states that may exist in materials such as oxide semiconductors do not appear to have been carried out to any extent in the literature; only a few speculations were found. It, also, is not known whether surface states may have a far greater effect at lower rather than higher temperatures, such as those required for thermionic emission. However, it must be recognized that collector materials may have fairly low temperatures in many types of thermionic converters. A detailed analysis of the possible effect of surface states on the thermionic constants of materials appears to be warranted.

Recently, experimental determinations of the temperature dependence of the work function of various high melting metal oxides and tungstates have been reported in the literature (35). The temperature coefficient for the oxides in many cases were found to have a positive value at temperatures below  $\sim 1400$ - $1600^{\circ}\text{K}$ , but showed a negative coefficient above these temperatures. The mechanism of emission was assumed to be connected with the presence of large quantities of free metal (donors) in the coating and this followed the theoretical prediction of the temperature dependence of the Fermi level as determined from classical statistical mechanics. The effects at the surface were assumed to be negligible. However, it should be pointed out that many problems appeared to arise in the conduction of these experiments and the close agreement between experimental values and calculated values may be quite coincidental. The coefficients that were determined for the tungstates were in the order of  $10^{-3}$  ev./deg. which, if fairly reliable, offers possibilities for the use of these solids at both low and high temperatures in thermionic converters. Table 5 (mostly taken from Reference (35) gives a compilation of  $\alpha$  for various oxide semiconductors.

**TABLE 5**  
**TEMPERATURE DEPENDENCE OF  $\phi$  FOR VARIOUS OXIDES**

Oxide	$\alpha$ ev/ $^{\circ}$ K	Temp. range for Measurements $^{\circ}$ K	Reference
(B <sub>a</sub> -S <sub>r</sub> )O	$3 \times 10^{-4}$	600-1000	36
BaO	$6 \times 10^{-4}$	369-1017	37
Sc <sub>2</sub> O <sub>3</sub>	$2.2 \times 10^{-4}$	1700-2000	35
Y <sub>2</sub> O <sub>3</sub>	$3.3 \times 10^{-4}$	1600-2000	35
La <sub>2</sub> O <sub>3</sub>	$8.8 \times 10^{-4}$	1800-2000	35
TiO <sub>2</sub>	$4.8 \times 10^{-4}$	1500-2000	35
ZrO <sub>2</sub>	$5.0 \times 10^{-4}$	1700-2000	35
HfO <sub>2</sub>	$4.8 \times 10^{-4}$	1500-2000	35
Ba <sub>3</sub> WO <sub>6</sub>	$1.3 \times 10^{-3}$	700-1300	35
Sr <sub>3</sub> WO <sub>6</sub>	$1.2 \times 10^{-3}$	900-1400	35
Ca <sub>3</sub> WO <sub>6</sub>	$1.1 \times 10^{-3}$	900-1400	35

The temperature coefficient of the forbidden band gap seems to be in the order of  $-10^{-4}$  ev./deg. and has been attributed mostly to a thermal expansion effect and phonon-electron interactions(38). In Table 5, a compilation of  $\frac{dE_g}{dT}$  for some well known semiconductors has been compiled.

**TABLE 6**  
**TEMPERATURE DEPENDENCE OF THE BAND GAP**  
**FOR VARIOUS SEMICONDUCTORS**

Material	$dE_g/dT \times 10^4$	Material	$dE_g/dT \times 10^4$ ev
Ge	-4.2	GaN	-3.9
Si	-2.7	SiC	-3.3
InSb	-2.7	Sb <sub>2</sub> Se <sub>3</sub>	-4.4

$\frac{dE_g}{dT}$  for most of these materials have been determined in the temperature region of 0°K to 373°K, with a linear relationship found at the upper temperatures. It is not known what the values may be at the higher temperatures that are necessary in thermionic converters since no measurements have apparently been made in this range, but it is certainly a factor which should be considered in the overall interpretation of the temperature coefficient of the work function.

In this section, the temperature dependence of the electron affinity in semiconductors has been neglected since it is assumed to be small, but this may not always be the case. This might be a fruitful area for investigation.

#### 4. Effect of Adsorbed Layers on the Work Function of Solids

##### a. Introduction

It has long been known that the introduction of certain gases and metallic vapors can influence the operation of a diode in two major directions. First they can influence the emitter and collector by raising or lowering their work functions and secondly, if a sufficient quantity of positive ions are formed, the space charge region between the emitter and collector may be largely neutralized. In the present discussion only the first effect will be considered.

When an atom is adsorbed at the surface of a solid a change in work function almost always occurs, the magnitude of which is dependent upon the degree and type of electron interaction between the metal and adsorbate. The mechanism of this charge transfer process is found to be dependent upon factors such as electron structure and surface properties of a substrate, the ionization potential and electronegativity of the adsorbent and adsorbate, the work function of the substrate, the extent of physical and chemisorption, and the degree of monolayer coverage on the surface of the adsorbent.

##### b. Physical Adsorption

In order to understand the basic mechanisms that determine the magnitude of the change in work function that may occur upon adsorption, it is necessary to understand the nature of the forces involved in the process and its dependence on the distance between the adsorbed atoms or ions and the adsorbent. Though the nature of these forces may be derived from fundamental wave equations, it is found to be convenient to treat the various forces involved as independent entities with each one contributing to the overall effect. These forces include the following: (1) dipole-dipole interaction, (2) dipole-quadrupole interaction, (3) quadrupole-quadrupole interaction, (4) electrostatic polarization of atoms or molecules by ions or dipoles, (5) the resonance exchange forces leading to covalent bonds (Pauling's theory), (6) the repulsion forces due to the inter-penetration of electron clouds. It should be emphasized that the extent of the contribution of these various forces will differ, depending largely upon whether the adsorbent is a dielectric, semiconductor, or a conductor. The first three forces mentioned above are the so called van der Waal's forces

(dispersion forces); their contribution to the attraction energy can be estimated from the following type of expression (39)

$$E_w = \frac{C}{r^6} - \frac{D}{r^8} - \frac{E}{r^{10}} \quad (1)$$

where C, D and E are constants which depend upon the nature of the atoms involved, and r is the equilibrium distance between the adsorbate and the surface. London (40) investigated the dipole-dipole interaction on the basis of quantum mechanics and showed the dependence of the attraction between two atoms upon the probability of various optical transitions which the atoms may make. Because of the connection with the phenomena of the dispersion of light, these attraction forces were called dispersion forces. C is thus defined as:

$$C = \frac{3\alpha_1 \alpha_2}{2} \cdot \frac{h\nu_1 \nu_2}{\nu_1 + \nu_2} \quad (2)$$

where  $\alpha_1$  and  $\alpha_2$  are the polarizability of the atoms involved and  $\nu_1$  and  $\nu_2$  are characteristic frequencies of the optical dispersion curve of the atoms; it has also been found that  $h\nu_1$  and  $h\nu_2$  are often approximately equal to the ionization potentials  $I_1$  and  $I_2$  of the atoms, and therefore if no data on the dispersion is available, C can be equated to:

$$\frac{3\alpha_1 \alpha_2}{2} \cdot \frac{I_1 I_2}{I_1 + I_2} \quad (3)$$

Other approximations for C have also been derived by various theoreticians; for example, Slater and Kirkwood (41) found that

$$C = \frac{3 e h^2}{4 \pi (m^* e)^{1/2}} \cdot \frac{\alpha_1 \alpha_2}{(\alpha_1/n_1)^{1/2} + (\alpha_2/n_2)^{1/2}} \quad (4)$$

where e and  $m^*$  are the charge and effective mass, respectively, of an electron;  $\alpha_1$  and  $\alpha_2$  are previously defined; and  $n_1$  and  $n_2$  are the number of

valence electrons in the outer shells of the atoms. Finally, Muller (42) found C as:

$$C = 6m^* c^2 \alpha_1 \alpha_2 \left( \frac{\alpha_1}{x_1} + \frac{\alpha_2}{x_2} \right) \quad (5)$$

where  $c$  = velocity of light and  $x$  = diamagnetic susceptibility. In Equation (1) approximate derivations for the constants D and E are arrived at in an analogous manner to that described for C (39).

Another important force to be considered in adsorption phenomena is the contribution of repulsion forces, first suggested by Born and Mayer (43) from the cohesive energies of alkali halides and oxides. These repulsion forces arise from the interpenetration of electron clouds of the atoms and increase strongly with decreasing distance between the atoms. A simplified empirical explanation for repulsion forces may be of the form:

$$E_{rep} = + \frac{b}{r^n} \quad (6)$$

where  $b$  and  $n$  are constant and  $r$  is the interatomic distance between the adatom and adsorbent.

When van der Waal's and repulsion forces along are considered the potential energy of two atoms attracting each other will be  $-E_w$  (from Equation (1)) +  $E_{rep}$  and will of course be at a minimum at the distance between the atomic cores when these two forces are balanced. Figure 7 shows a typical adsorption curve illustrating this.

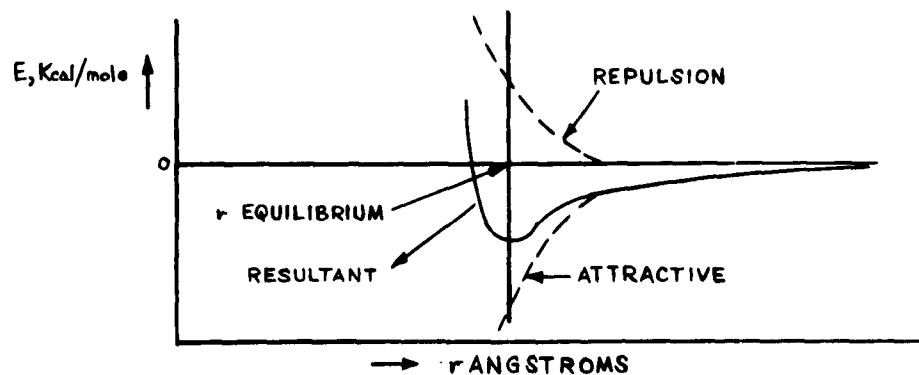


Figure 7 - E as a Function of r

In calculating the energies involved in van der Waal's forces the last two terms of Equation (1) have been frequently omitted since the assumption is made that they are approximately counterbalanced by the contribution of repulsion forces. The energy involved is then determined solely by  $\frac{C}{r^6}$  alone.

The discussion as far has dealt with the interaction of two atoms; however, the total attraction between an adsorbed atom and a surface can be obtained in a general case by a triple integration calculation similar to that of Polanyi and London (44) (once again using the first term of Equation (1).

$$E_w = \iiint - \frac{C}{r^6} N_3 dr = \frac{N_3 \pi C}{6} \frac{1}{r_0^3} \quad (7)$$

where  $N_3$  is the number of atoms of the adsorbent per cubic centimeter and  $r_0$  is the shortest distance between the adsorbed atom and the surface. Thus, it is seen that the decrease in potential energy due to van der Waal's forces in the case of adsorption on a surface is inversely proportional to the third power of  $r_0$ . Although Polanyi and London's treatment of the interaction between the non-polar molecule and a surface is apparently applicable only to adsorbents that are non-conductors such as ionic crystals, Margenau and Pollard have considered that dispersion forces in metals can resemble those found for dielectrics (47).

The interactions between a metal and a non-polar molecule was first treated by Lennard-Jones (45) who assumed that the metal was a completely polarizable solid and therefore it would be possible to calculate the interaction between the conducting surface and the fluctuating dipole of the gas molecule by the method of electrical images. His method was partly quantum-mechanical since he considered the image potential in the metal acting upon the gas molecule as a perturbation. Bardeen (46) improved the calculations of Lennard-Jones by treating the metal substrate as well as the adsorbed molecule quantum-mechanically. For physical adsorption on monovalent metals, Bardeen's attractive energy is one half that calculated by Lennard-Jones, but for metals with higher electron densities and with an adatom of small ionization potential, Bardeen predicted values which approximate those predicted by Lennard-Jones.

Margenau and Pollard (47) have raised serious objections against the use of the electrical image picture just described. They considered that the inducing fields of the continually changing dipoles in a nonpolar molecule change so rapidly that the conduction electrons in the metal are unable to follow their movements. With respect to van der Waal's forces the adsorbent conductor therefore behaves as a dielectric. The magnitude of van der Waal's attractive force is estimated as the sum of  $E_1$  and  $E_2$ , where  $E_1$  results from the polarization of the metal by the continually changing dipole in the adsorbed atom and  $E_2$  arises from the polarization of the adsorbed atom by the electron movements in the metal. Their final expression is

$$E_w = \frac{e^2 \alpha_o}{16 r_o^3} - \frac{h n_o}{m_e r_o} + \frac{C_B}{r_s} \quad (8)$$

where  $n_o$  is the number of conduction electrons per cc in the metal,  $\alpha_o$  is the polarizability of the adatom,  $r_s$  is the radius of a sphere encompassing a free electron in the metal,  $C_B$  is a dimensionless constant, slightly dependent upon  $r_s$  and approximately equal to 2.6.

With regard to the above discussion, it should be emphasized that these estimations of interaction forces are still somewhat in the formulative stage, due in some degree to the fact that the repulsive potential has not been analyzed sufficiently. Also, in the calculations of the attractive forces the surface has been idealized as a mathematical plane and the detailed distribution of electrons and ion cores has been mostly ignored in the interest of simplicity. It should be realized that in the theoretical calculation of adsorption energies the lack of exact knowledge concerning the real distance of the adsorbed atom or molecule from the adsorbent is an important parameter which frequently must be taken into account. Quite often this distance is assumed to be the sum of the radii of the adsorbed atom and a surface atom, or just the distance related to the radius of the adsorbate. Since the adsorption force depends on the polarizability of the adsorbent the actual distance between the two atoms might be somewhere between these values. Therefore, depending on the assumption of where the polarizability starts, this distance may actually vary by a factor of about 2. The latter considerations are actually borne out by experimental observations that indicate



that physical adsorption (i. e. , adsorption of rare gases on metals) may actually result in stronger interaction forces that would otherwise be estimated from the previous equations. One simplifying explanation for this occurrence is the assumption that a positive dipole layer (simulating a parallel plate condenser) arises from the redistribution or polarization of the electron charge at the adsorbent surface. De Boer (39) and Ehrlich (48) have estimated the extra contributions of the polarization effect to the binding energy by assuming a simple electrostatic contribution which is caused by the polarization of an atom by an electrostatic field,  $F$ . The extra binding energy is then  $\Delta E = 1/2 \alpha F^2$ , where  $\alpha$  is the polarizability of the adatom. The effective field at the surface is estimated from the experimentally observed dipole moment,  $\mu$ , which is equivalent to  $\alpha F$  and is related to change in work function as follows:

$$\Delta \phi = \pm 4 \pi \Delta (\epsilon_m \theta \mu) \quad (9)$$

where  $\Delta \phi$  is the change in work function  
 $\epsilon_m$  is the total number of sites per  $\text{cm}^2$  which may be available to the adsorbate  
 $\theta$  is the fraction of  $\epsilon_m$  which is available to the adsorbate, or the degree of monolayer coverage on the surface  
 $\mu$  is the dipole moment per atom and is equal to the product of electronic charge and the distance between the positive and negative layers.

One representative calculation showing the above relationships is that for the adsorption of xenon on tungsten, which Ehrlich has found to decrease the work function  $\sim 0.7$  volt; this should correspond to  $2 \times 10^{14}$  adatoms/ $\text{cm}^2$ , and would allow a dipole moment per atom of 0.93 Debyes, an electrostatic field of  $2.3 \times 10^5$  esu and an increase in the binding force of 1.6 kcal/mole. Since the heat of desorption has been previously determined experimentally as  $\sim 8$  kcal/mole, this induced polarization or change in work function is thus seen to contribute approximately 20% to the total binding energy; the van der Waal's

adsorption force being responsible for the other 80%. A somewhat different approach to the "interaction" problem has been postulated by Mulliken (49) who also conceived that in addition to dispersion forces, some lowering of the potential energy of an adatom at a metal surface may arise due to the redistribution of the electron bond at the surface. However, he considered that this phenomenon occurred when an electron transferred from the neutral adsorbate to the metal, thus setting up various exchange reactions with the resulting ion curves. The apparent key to this approach is the assumption that although most metals show a fairly substantial reduction in work function (positive dipole layer), a chemical bond is not actually formed in the sense that it probably does in a chemisorption process (on the basis of electronegativity which can be introduced if chemical bonds were considered, the dipole layer would have to be negative which is not the case that is observed experimentally). The fact that the transition metals such as tungsten possess d-orbitals of low energy indicates the feasibility that this type of electron transfer may readily occur in physical adsorption. In this way, the positive double layer in physical films is, in a way, a continuation of the double layer at the surface of the clean metal.

#### c. Chemisorption

In the discussion so far, the mechanism of physical adsorption has been mainly considered. The other type of bonding which is of importance in thermionic energy conversion, deals with the phenomenon of chemisorption. The distinction between physical and chemisorption is not always clearly defined: however, some of the differences may be summarized as follows:

1. In chemisorption, there appears to be no question concerning the fact that at least a partial transfer of electrons occur between the adsorbent and adsorbate.
2. Chemical bonds are usually much stronger than physical forces of attraction since the heat of adsorption of the latter is of the same order of magnitude as the heats of condensation of gases, ( $\sim 8$  kcal/mole). However, it should be emphasized that some overlapping may occur at times and that this differentiation may not always be infallible.
3. Another difference to be considered is the fact that chemisorption possess a certain degree of specificity which physical adsorption does not.

Under the correct conditions of temperature and pressure physical adsorption takes place on all surfaces while chemisorption depends on the chemical affinity between the particular adsorbent and adsorbate. In other words not all surfaces, even when clean, are active in chemisorption.

4. Chemisorption, being a chemical reaction, may require an appreciable activation energy. In that case it will proceed at a reasonable rate only above a certain minimum temperature. With van der Waal's forces, no energy of activation is required and the gas molecules are adsorbed as rapidly as they reach the surface. Under conditions under which the two adsorptions occur simultaneously, they can usually be separated on the basis of the difference in reversibility with respect to temperature and pressure. The removal of chemisorbed gas from the surface is usually difficult, while physical adsorption is readily reversible. However, one possible exception to the latter appears to arise during ion bombardment of surfaces whereby ions such as argon or helium may become imbedded in the solid and actually may not be evolved in certain instances until a temperature of  $1000^{\circ}\text{C}$  is reached. It should also be pointed out that the work function of certain ion bombarded surfaces can certainly be affected by this occurrence.

As seen previously, chemisorption involves electron transfer between adsorbate and adsorbent with the apparent formation of chemical bonds similar to those occurring in bulk materials. Since the latter can be described in terms of ionic, covalent, and partially covalent bonds, the same definitions have been applied to adsorption phenomena where the type and strength of bonding between surface and adatom has a major effect on the heat of adsorption, and thus determines the dipole moment that is created. This leads to a parameter of major importance in thermionic phenomena -- the relationship between the change in work function of a solid and a partially chemisorbed monolayer on its surface.

It is realized that it may be dangerous to attempt to closely correlate chemisorption behavior with observed and theoretical bulk parameters, but this appears to be the best course to follow. Therefore, there are two theories of the metallic state which are utilized in a study of chemisorption. They are (1) the Electron Band Theory which is based on the concept of a free electron gas obeying the appropriate statistical mechanical rules, and (2) the

Valence Bond Theory, after Pauling (50), which takes the opposite view, namely that the properties of metals are adequately described in terms of essentially covalent bonds between adjacent atoms. The Electron Band Theory, or quantum mechanical approach, considers that electrons in metals retain much of the s, p, and d orbital characteristics, which in an isolated atom are definite and single valued energy levels. However, in a crystal each level is compelled by the Pauli exclusion principle to lose its identity and to be replaced by a corresponding energy band. In particular the bands of the valency electrons may overlap so that electrons may be exchanged between two or more bands; this situation characterizes all metals except those of Groups IA and IIA. It is then necessary to consider the probability of finding an electron at any energy within the permitted band. This leads to calculations of the density of states distribution and the Fermi energy. Electronic conductors appear to be classified into two types of solids — those having low-lying, unfilled d-orbitals and those without such orbitals (s, p). The chemisorption characteristics of both types are found to be different from each other in many ways. For example, only d-metals (transition type metals) appear to chemisorb hydrogen and nitrogen. Transition metals, which are of interest in thermionic converter programs, have a probable band structure consisting of a broad s-band containing a low maximum density of states level and a narrow d-band which results in a much higher maximum level density. As electrons are progressively added in building up a long period, they first go into the s-band and thereafter into both bands. The important distinguishing feature of transition metals are the possession of incomplete d-bands which take part in the chemisorption process.

Because of the complex structure of the d-band exact quantitative knowledge concerning the electron structure of most transition elements have been lacking, and for this reason an alternative approach, that of the valence band theory has been derived. In this theory, it is supposed that s, p and d-electrons are all capable of taking part in cohesive bonding and that the actual orbitals are available for hybrids. The valence band approach has one advantage in that it is possible to consider emergent orbitals with unpaired electrons at metal surfaces and it also allows estimations to be made of the percentage of d-character in bonds between transition atoms.

It has been borne out by adsorption data that a high d-character favors covalent bond formation with chemisorbed atoms while a low-d-character favors more ionic type bonding.

Dowden (51) utilized statistical thermodynamics for both the Electron Band and the Valence Bond Theory to predict various factors which favor electron transfer processes between an adsorbate and an adsorbent. His equations allow discussion of the probability of positive ion, negative ion, or covalent bond formation occurring on metal surfaces. For positive ion formation, the ratio of the ionized to unionized species is given as follows:

$$C_{A^+}/C_A = \frac{f(A^+)}{f(A)} \exp \left[ - \left( I' + \mu_e^m \right) / kT \right] \quad (10)$$

where

$$I' = I + \Delta\mu^+$$

and

$$\mu_e^m = -\phi - 1/6 \pi^2 k^2 T^2 \left( \frac{d \ln N(E)}{dE} \right)_{E = -\phi}$$

$f(A^+), f(A)$  = partition functions for ionized and neutral particles

$\mu_e^m$  = thermodynamic potential per metal electron per unit volume.

$I$  = ionization potential of the neutral particle

$\Delta\mu^+$  = adsorption energy of the ion

$\phi$  = work function of adsorbent

$N(E)$  = number of permitted states in energy band

The latter equation has dealt with the adsorption of electropositive atoms on a surface. In the case of the adsorption of electronegative atoms such as  $O_2$ ,  $CO$ ,  $N_2$ , etc., negative ion formation is likely since the tendency is for an electron to be removed from the highest occupied level in the metal substrate to the lowest unoccupied level of the adsorbate. For the most part the conditions that have been discussed for positive ion formation are reversed. Therefore, for negative ion formation:

$$C_B^- / C_B = \frac{f(B^-)}{f(B)} \exp \left[ - \left( E_a' - \mu_e^m \right) / kT \right] \quad (11)$$

where  $E_a' = E_a + \Delta\mu^-$

$E_a$  = electron affinity of the adsorbent

$\Delta\mu'$  = adsorption energy of the anion

Negative ion formation will thus be favored by a low value of  $\phi$  and a large negative value of  $\frac{d \ln N(E)}{dE}$  at the Fermi level. Finally, covalent bond formation is found to be favored by (1) large values for  $\phi$ , (2) large positive values of  $\frac{d \ln N(E)}{dE}$ , and (3) the presence of unfilled atomic orbitals.

With tungsten as an adsorbent it appears that the maximum amount of ionization occurs when an atom such as cesium (ionization potential 3.89 ev.) is brought to the surface of a polycrystalline tungsten (work function 4.56 ev.). Utilizing quantum-mechanical considerations only, it might appear that the mechanism of ionization begins when the cesium atom upon approaching the tungsten surface broadens out into a band, the magnitude of which depends upon the adsorbate band structure. At equilibrium, the energy states which would contribute to the probability of a valence electron being found near the Cs atom core, lie well above the states which are normally filled. Therefore, the valence electron charge distribution about a Cs atom will be quite small and the electron has a marked tendency to occupy one of the lower energy levels in the tungsten lattice — in effect the atom is ionized.

Other elements whose ionization potentials are also smaller than cesium are potassium, rubidium, and possibly thorium, and it would be expected that these elements would show considerable ionization upon contact with tungsten. However, as first pointed out by Gurney (52), it is probable that some degree of positive ionization of adsorbed atoms can occur even when their ionization potentials exceed the work function of the adsorbent. Since the relative electron charge distribution is determined by the potential fields around the lattice ions and around the core of the adatom, it may be better to compare the ionization potentials of the two atoms than by comparing the work function of the solid with the ionization potential of the adsorbate. Thus, elements such as Ca, Sr, and Ba all have ionization potentials greater than the work function, but less than the I. P. of W and they therefore may be partially ionized on W.

The next step in understanding the chemisorption process is to consider the actual forces involved in the formation of an adsorbate-adsorbent bond. When a highly polarizable atom is adsorbed on a metallic surface, the electron charge of the ion will polarize the metal in such a way that the phenomena may be described as if an electric charge of opposite sign were formed (so-called electrical image) at a distance below the surface equal to the distance,  $r$ , between the actual inducing charge and the metal surface. The image force is given by:

$$F_i = \frac{n_1^2 e^2}{(2r)^2} \quad (12)$$

where  $e$ , is the charge of an electron and  $n_1$ , denotes the number of elementary charges of the ion.

In addition to the above considerations it should be noted again that an ion adsorbed on a metal surface will be attracted by the usual van der Waal's forces and also repelled by repulsion forces thus actually balancing the attraction forces at an equilibrium distance,  $r_0$ . The value of  $r_0$  derived in the above manner and in conjunction with the heat of adsorption of the  $\text{Cs}^+$  ion has been found to be  $1.74^\circ\text{A}$  which indicates that the boundary of the region of ideal polarization starts at a plane through the center of the surface atom of tungsten. However, recently the reality of the electrical image has been questioned (53) and it is considered that the effective dipole length is the distance between the positive charge and the surface. Thus it can be seen that the correct definition for  $r_0$  may still be in some doubt.

If it is assumed that ions actually exist on the surface of a metal and the classical image law holds, the total heat of adsorption of an atom that becomes ionized can be estimated by the following equation:

$$E = \phi - I + \frac{n_1 e^2}{4r} \quad (13)$$

where  $\phi$  is the substrate work function and  $I$  is the adatom ionization potential. Agreement with experimental results for the alkali metals has been reasonably good, considering that  $\frac{e^2}{4r}$  may be modified by various polarization forces, van der Waal's forces, and repulsion forces which have been mentioned previously.

In regards to chemisorption, it appears an analogy can usually be made that each adatom constitutes a dipole which is aligned perpendicular to the surface with the resulting system approximating a double charge layer or capacitor. The magnitude of this dipole layer will of course depend upon the density of dipoles created on the surface and the distances between the positive and negative charges. The effect of this dipole layer on the work function can be calculated using the equation

$$\Delta\phi = \pm 2\pi \Delta (\epsilon_m \theta \mu) \quad (14)$$

which is similar to that given in the previous discussion on physical adsorption. The possibility of using this equation for both types of adsorption arises if chemisorption can be described strictly in terms of dispersion and polarization forces, which has been attempted by Dröschler (54). However, in the case of chemisorption it has been found much easier to deal with the type of chemical bond which is formed, since this has been related more directly to the heat of adsorption, and thus the work function. As previously mentioned the type of bond formed in the chemisorption process can vary from that of highly ionic to that of highly covalent, just as normal chemical bonds behave in bulk solids. This leads to various degrees of electron transfer and interactions which have an important effect on the parameters which are being investigated. Equation (14) is of major importance in adsorption phenomena and can serve equally well, in an empirical manner, in describing the adsorption of adatoms which tend to increase or decrease the adsorbent work function. The sign of  $\Delta\phi$  depends upon whether dipoles are formed which have positive or negative charges directed away from the surface. However, one word of caution should be noted in the use of Equation (14) — from the earliest work of Langmuir and his co-workers till the present time there has been a conflict of opinion concerning whether  $\Delta\phi = \pm 4\pi \epsilon_m \theta \mu$  or  $\pm 2\pi \epsilon_m \theta \mu$ . Langmuir uses the latter equation for both highly ionic adsorption as well as highly covalent adsorption on a surface, while many investigators including de Boer (39) and Higuchi et al. (53) have used  $4\pi$  for ionic and  $2\pi$  for covalent adsorption. Though, recently de Boer appears to have gone back to some of Langmuir's original concepts. It is therefore seen that the dipole moment,  $\mu$ , may have



two values, one of which will be half that of the other. In conjunction with the latter problem, it should be reiterated that exact information concerning the distances involved between the center of an atom and its counterpart on the adsorbent surface is in considerable doubt. The present investigators tend toward the Langmuir formula ( $2\pi$ ) for initial adsorption on a surface and believe that the values for the dipole moment calculated from the equation are more near the correct ones (although it should be realized that Higuchi considered that the effective dipole length is just the distance between the positive charge and the surface). It is also felt that the dipole moment calculated in that manner should give a further indication of the degree of ionicity present in a particular adsorbate - adsorbent bond. An example of this may be seen from Langmuir and Taylor's data (55) where 7% coverage of a tungsten filament by cesium resulted in a decrease in the work function of 0.64 volts. An investigation of the crystal habits of the tungsten filament revealed that the 110 plane was favorably exposed thus giving a value for the atomic density on the surface of  $1.425 \times 10^{15}$  atoms/cc. Since the diameter of the cesium atoms is exactly twice that of tungsten, and because of the tendency of the adatoms, under the strong forces exerted by tungsten, to occupy definite elementary spaces on the surface, it was concluded that the maximum number of cesium adatoms is one-quarter the number of tungsten atoms. Thus, the true value of  $\zeta_m$  is  $3.563 \times 10^{14}$  atoms/cc. The value of  $\mu$  from Equation (14) is then found to be:

$$\mu = \frac{0.64}{300 \times 2\pi \times 3.563 \times 10^{14} \times .07} = 13.6 \times 10^{-18} \text{ esu or } 13.6 \text{ Debyes}$$

In the theoretical case of 100% ionization, the value of  $\mu$  from  $ed_0$  ( $d_0 = 2 \times$  ionic radius) would be approximately 17.2 Debye. This would give a degree of ionicity for the particular Cs-W bond being considered as  $\frac{13.6}{17.2} \times 100 = 79.7\%$ . Partial monolayer coverages for other adsorbates, which give a positive surface potential, can probably also be described in the above manner.

Although the tendency in adsorbate-adsorbent electron transfer is for an electron to be removed from the highest occupied level (Fermi level) in the

metal to the lowest unoccupied level of the adsorbate, it is actually not at all certain whether the relation  $\Delta\phi = \pm 2\pi \epsilon_m \theta \mu$  is always meaningful due to the lack of knowledge of the exact length between the adatom and the adsorbent. It is known from Pauling's work (50) that the bond length depends upon many factors such as the coordination number (ligancy) between atoms in a solid, and the resonance exchange energy. One problem that exists in relating electropositive and electronegative adsorption to each other appears to be the fundamental question as to whether complete ionization or complete covalency in a bond should be the base from which comparisons might be made. The concept of the deviation from complete covalency in a chemisorption bond was initiated by Eley (56) who utilized Pauling's calculation of the bond energy of covalent molecules:

$$D(M-B) = 1/2 [D(M-A) + D(B-B)] + 23.06 (X_a - X_b)^2 \text{ Kcal/mole} \quad (15)$$

where  $D$  is the dissociation bond energy,  $M$  is the metal atom, and  $B$  is the adatom.  $D(M-M)$  and  $D(B-B)$  can frequently be estimated as  $1/6$  the sublimation energy of the metal or from known values.  $X_a$  and  $X_b$  are the electronegativities of  $A$  and  $B$  respectively. Comparisons between experimental theoretical values for  $D(M-B)$  appear to be quite good for smaller values of  $X_a - X_b$ . From the above relationship and Pauling's theory an assumption may be made that  $X_a - X_b$  equals the dipole moment,  $u$ , of the bond formed between them with the result that the surface potential  $\Delta\phi$  is considered to be  $2\pi \epsilon_m \theta (X_a - X_b)$ . With regards to the use of the surface potential equation, it should be emphasized that for reasonably accurate results the dipole moment at zero coverage,  $\mu_0$ , is required, since on the basis of various experiments it appears that with increasing coverage, adsorbed dipoles generally begin to react with each other (depolarization effect) and reduce the dipole moment per adatom. The latter apparently decreases at a greater and greater rate with increased coverage and seems to affect highly ionic bonding much more than highly covalent bonding. However, Eley's equation pertaining to the covalent bonding concept makes no distinction between the dipole moment per atom between  $\theta = 1$  and  $\theta = 0$ .

With cesium absorption on tungsten the maximum reduction in average work function of approximately 3 ev. takes place if the surface covered is

only 0.67 of a monolayer, because in spite of an increase in cesium concentration above this critical value, the average dipole moment per unit area actually decreases. An equation estimating the total depolarization effect on  $\mu$  with increased coverage was given by

$$\mu_{\theta} = \mu_0 / 1 + 9 \alpha \theta \zeta_m^{3/2} \quad (16)$$

where  $\mu_0$  is the dipole moment resulting from the first atoms adsorbed on a bare tungsten surface,  $\mu_{\theta}$  is the dipole moment per bond at a particular coverage,  $\alpha$  is the electronic polarizability of the adsorbate and  $\theta$  and  $\zeta_m$  have been previously defined. The value of  $\alpha$  can only be estimated and may in fact have a value anywhere from  $7 \times 10^{-24}$  to  $40 \times 10^{-24}$  depending on the varying type of bonding which occurs and on several other factors. Thus, Equation (16) can only be used in a very qualitative manner. However, it does indicate that extremely large depolarization effects can occur at the higher coverages with ionic type bonding with probably an infinity range of values occurring all the way to completely covalent bonding.

In connection with the change in surface potential that occurs upon adsorption and increased coverage, it should be pointed out that a continuous decrease in the heat of adsorption occurs irrespective of the sign of the dipole layer that is formed as the amount of surface coverage increases. In the case of a continuous increase in work function with adsorption more work is apparently required to transfer electrons to the substrate while with positive dipole formation less energy is gained during succeeding adsorption of atoms. In the absorption of cesium on tungsten, Taylor and Langmuir (55) tried to represent  $\Delta H$  as a function of  $\theta$  by the following empirical equation:

$$\Delta H = \frac{64}{1 + 0.714 \theta} \text{ Kcal/mole} \quad (17)$$

This equation appears to hold reasonably well between  $\theta = 0.06$  and  $\theta = 0.60$ . At  $\theta$  values lower than 0.06 the heat of adsorption was found to decrease more strongly with increasing coverage than was calculated by the equation. This deviation from the empirical equation was explained by Taylor and Langmuir by the presence of some excessively active areas on the tungsten surface, which would be eventually covered.

#### d. Importance of Crystallographic Planes

During the last decade (as indicated previously) the importance of the effect of different crystallographic planes on electron emission and adsorption phenomena has become of prime consideration. It has been found that when gaseous atoms strike different planes of a particular crystal at a constant rate, the work function and therefore the thermionic emission changed at different rates depending on the particular crystallographic plane that was investigated. Also, if the temperature of the surfaces was raised uniformly it was noted that the properties of some planes changed much more rapidly than others indicating that the heats of adsorption and desorption were dependent upon crystallographic orientation.

This is certainly not surprising due to the fact that the density of adsorbent surface atoms and the work function of the bare surface may vary considerably from plane to plane. For example, in comparing a 110 tungsten plane with a density of  $1.4 \times 10^{15}$  atoms/cm<sup>2</sup>, to that of a 411 plane with a density of  $4.8 \times 10^{14}$  atoms/cm<sup>2</sup>, it can be seen that one monolayer of adsorbate would be completed with only one third as many adatoms as on a 110 plane. At the same time the work function of the clean 110 plane may be as high as 5.5-6.0 ev. whereas the work function for the 411 (also 310) planes appears to be as low as 4.2 ev. A rough approximation to follow in predicting the effect of adsorption on various planes of tungsten is that low index planes will generally show a greater change than that occurring on high index planes. However, it should be recalled that in the chemisorption of electronegative atoms the metal tends to transfer electrons to the adsorbate and a low adsorbent work function favors this process; thus it is found that several competing factors have to be taken into account before exact predictions can be made in all cases.

Chemisorption on surfaces other than those of metals have been studied, mostly on oxides or salts. One school of thought has considered this phenomena mainly from the chemical point of view, whereby all of these solids are described as ionic crystals and no distinction is made between semiconductors and insulators. In this theory it is considered that during chemisorption, surface atoms or ions are produced which possess lower valencies than those occurring in the adsorbent before adsorption. It is the creation of these lower valency ions which promote the transfer of electrons from the adsorbant to adsorbate.

The other point of view considers that the problem of the adsorption of a gas on a semiconductor will bear a close analogy to the problem of a semiconductor-metal contact which has been quite thoroughly investigated theoretically (28). This theory deals mainly with the creation of a space charge which continually builds up in the electronic boundary layer between the substances in contact with each other. As a result of this space charge the potential energy of electrons in the semiconductor becomes modified, and in transferring from the semiconductor to the adsorbate electrons have to surmount a potential barrier. Beyond a certain point chemisorption can no longer proceed with a decrease in free energy and few additional atoms will stick to the surface for any length of time. For example, in the adsorption of  $O_2$  on many oxides it is found that only several percent of a chemisorbed monolayer can actually be determined experimentally.

#### e. Adsorption Data

Table 7 shows a compilation of experimentally determined adsorption data from the literature. The direction and magnitude of work function changes are indicated together (in most cases) with the type of experimental technique and substrate temperatures used in obtaining the data. However, a theoretical interpretation of the results, especially that obtained in earlier work, should proceed with caution since most investigations have yielded surface potentials that were thought to arise from nearly complete monolayers (depolarization effects may be considerable). Ironically, in some cases the coverage may actually be far less than expected for the particular gas being studied, with an additional possibility that impurity atoms may contribute much of the remainder of the monolayer (58). For example, it appears that at any temperature nitrogen need not completely cover a tungsten surface and that the sticking coefficient becomes vanishingly small when  $1/2$  of the available sites are filled. The remaining sites may still be occupied by other gases such as oxygen, hydrogen or carbon monoxide. At lower temperatures additional molecular nitrogen may be adsorbed. This phenomenon appears to be more pronounced with oxygen on tungsten than with the other gases, but the possibility of selective adsorption should be considered in all cases. However, it must be assumed that the more recent investigations are generally more accurate than older experiments due in large measure to the development

of the latest techniques in obtaining an ultra-high vacuum (insuring cleaner surfaces) and improved methods of purifying and analyzing gases and solids.

In this section, an introduction into adsorption phenomena has been presented with emphasis on the importance of understanding the properties of surfaces as distinct from those of bulk solids. The effects of various types of adsorption on the operating characteristics of a thermionic energy converter is indicated and the possibility is seen to exist that in the future surfaces may be utilized more than in the past in the operation of energy conversion devices.

TABLE 7  
ADSORPTION DATA FOR ELEMENTS

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev. )	Year of Measurement	Method Used for Measurement	Reference	Remarks
W	Cs	-3. 0	1932	Thermionic	59	Filament~1200°K
"	Cs	-3. 06	1940	Field Emission	73	
"	Cs	-2. 8	1929	Contact Potential	60	Filament~300°K
"	Cs	-2. 8	1938	Photoelastic	61	
"	Cs	-3. 03	~1953	Thermionic	62	Filament, Additional information is scarce
"	Cs	-3. 0	1940	Field Emission	93	
"	O-Cs	-3. 1	1929	Contact Potential	60	Filament, 300°K
"	O-Cs	-3. 13	~1953	Thermionic	62	Filament, Additional information is scarce
"	Ba	-2. 4	1932	Thermionic	63	Filament, ~1100°K
"	Ba	-2. 70	1955	Thermionic Radioactive Tracers	64	Ribbon, 100 plane 900-1100°K
"	Ba	-2. 05	1961	Ionization	65	~900°K
"	Ba	-2. 93	1959	Thermionic	66	Radioactive Tracers
"	Ba	-2. 93	~1953	Thermionic	62	Filament, Additional information is scarce
"	Ba	-2. 93	1956	Thermionic	67	
"	Ba	-2. 87	1940	Field Emission	73	
"	O-Ba	-3. 19	1934	Thermionic	68	

Table 7 (Cont.)

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev.)	Year of Measurement	Method Used for Measurement	Reference	Remarks
W	O-Ba	-3.23	~1953	Thermionic	62	Filament, Additional information is scarce
"	Sr	~ -2.40	1955	Thermionic	64	Ribbon, 100 plane 900-1100°K
"	Sr	-1.90	1961	Contact Potential	65	~ 900°K
"	Th	-1.7	1937	Contact Potential	69	Filament, ~1000°K
"	Th	-1.5	1929	Contact Potential	60	
"	Th	-1.86	~1953	Thermionic	62	Filament, Additional information is scarce
"	Th	-1.64	1933	Thermionic	74	
"	Na	-2.8	1937	Contact Potential	70	Filament, 300°K
"	O-Na	-2.82	1929	Contact Potential	60	
"	K	-3.0	1940	Field Emission	73	
"	K	-2.9	1937	Contact Potential	70	
"	K	~ -2.80	1938	Photoelectric	61	
"	Ca	-2.32	1944		75	
"	Ca	-1.70	1961	Contact Potential	65	~900°K
"	Li	-3.7	1929	Thermionic	76	
"	Mg	-0.75	1961	Ionization	65	~900°K
"	Be	No Change	1961	Ionization	65	~900°K
"	La	-1.86	~1953	Thermionic	62	Filament, Additional information lacking



Table 7 (Cont. )

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev. )	Year of Measurement	Method Used for Measurement	Reference	Remarks
W	Ce	-1. 86	~ 1953	Thermionic	62	Filament, additional information lacking
"	u	-1. 76	~ 1953	Thermionic	62	Filament, additional information lacking
"	$\lambda$	-1. 86	~ 1953	Thermionic	62	Filament, additional information lacking
"	Zr	-1. 46	1958	Thermionic	93	
"	Zr	-1. 43	~ 1953	Thermionic	62	Filament, additional information lacking
"	BaO	-3. 53	1956	Thermionic	67	
Mo	Cs	-2. 59	1961	Thermionic	71	Filament, ~1000°K
"	CsF	-2. 86	1961	Thermionic	71	Filament, ~1000°K
Mo	Th	~ -1. 64	~ 1953	Thermionic	62	Filament, additional information lacking
Ta	Th	~ -1. 62	~ 1953	Thermionic	62	Filament, additional information lacking
"	Th	~ -1. 60	1944	Thermionic	75	
Ni	CsF	-3. 56	1961	Thermionic	72	Slab, 500-800°K
"	Cs, CsH, H	-3. 96	1961	Thermionic	72	Slab, 500-800°K
Au	Ba	-2. 16	1956	Thermionic Radioactive Tracers	67	

Table 7 (Cont.)

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev.)	Year of Measurement	Method Used for Measurement	Reference	Remarks
	BaO	-1.36	1956	Thermionic	67	Radioactive tracers
Ge	Cs	~ -3.6	1929	Thermionic and Contact Potential	76	~600-800°C
"	Ba	-2.4	1956	Thermionic	67	Radioactive tracers
"	BaO	-1.2	1956	Thermionic	67	Radioactive tracers
W	O <sub>2</sub>	+1.60	1941	Contact Potential	77	
"	O <sub>2</sub>	+1.70	1935	Contact Potential	78	Filament
"	O <sub>2</sub>	+1.70	1935	Field Emission	79	1000°K
"	O <sub>2</sub>	+1.71	1939	Contact Potential	80	
"	O <sub>2</sub>	+1.74	1937	Contact Potential	81	Filament, 1270°K
"	O <sub>2</sub>	+1.89	1951	Contact Potential	82	
"	O <sub>2</sub>	+1.90	1955	Contact Potential	83	Film substrate, 293°K
"	O <sub>2</sub>	+1.90	1957	Field Emission	84	
"	O <sub>2</sub>	+1.7	1960	Contact Potential	85	~2 monolayers adsorbed?
"	O <sub>2</sub>	+2.10	~ 1958	Field Emission	91	300°K, pressure 5x10 <sup>-8</sup> mm Hg
"	N <sub>2</sub>	+0.50	~1955	Contact Potential	83	
"	N <sub>2</sub>	+1.38	1937	Contact Potential	86	Thin film, 293°K
"	N <sub>2</sub>	+1.40	1937	Contact Potential	86	T > 700°K

Table 7 (Cont.)

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev.)	Year of Measurement	Method Used for Measurement	Reference	Remarks
W	N <sub>2</sub>	-0.1	1961	Field Emission	87	~293°K
"	N <sub>2</sub>	+0.22	1956	Photoelectric	88	~183°C, effect was attributed to the presence of a polarized molecular layer containing N <sub>2</sub> <sup>+</sup> ions
"	N <sub>2</sub>	-0.06	1956	Photoelectric	88	
"	N <sub>2</sub>	+0.35	1958	Photoelectric	89	Ribbon, 113 plane, ~300°K $\Delta \phi$ continued to rise beyond this point to +0.98 ev., but apparently phenomena may be due to selected impurities being adsorbed
"	N <sub>2</sub>	+0.50	1958	Field Emission	90	~305°K, pressure $2 \times 10^{-8}$ mm Hg
"	N <sub>2</sub>	-0.20	1958	Field Emission	90	80°K, pressure $3 \times 10^{-9}$ mm Hg
"	N <sub>2</sub>	+0.30	1958	Field Emission	91	300°K, pressure $5 \times 10^{-8}$ mm Hg
"	N <sub>2</sub>	+0.54	1960	Contact Potential	92	300°K, pressure $\sim 10^{-6}$ mm Hg

Table 7 (Cont.)

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev.)	Year of Measurement	Method Used for Measurement	Reference	Remarks
W	N <sub>2</sub>	- .1 to -.3	1961	Field Emission	87	300°K
"	N <sub>2</sub>	+0.50	1950	Contact Potential	94	Pressure ~1.5x10 <sup>-3</sup> mm
"	CO	+0.86	1957	Photoelectric	95	113 plane
"	CO	+0.8	1959	Field Emission	96	110, 111 plane ~625°K, both planes resulted in same change
"	CO	+0.5	1961	Field Emission	93	300°K, pressure 4x10 <sup>-8</sup> mm
"	CO	+0.7	1961	Field Emission	93	80°K, pressure 6x10 <sup>-9</sup> mm
"	CO	+0.86	1939	Photoelectric	97	
"	H <sub>2</sub>	+0.48 to +0.65	1952	Contact Potential	98	Thin film, 83°K
"	H <sub>2</sub>	+0.50	1950	Contact Potential	99	Thin film, 293°K
"	H <sub>2</sub>	+0.55	1957	Field Emission	100	
"	H <sub>2</sub>	+1.04 to +1.26	1937	Contact Potential	101	Filament
"	H <sub>2</sub>	-0.17 to -0.47	1948	Contact Potential	102	Glow discharge
"	H <sub>2</sub>	~+0.5	1960	Contact Potential	103	
"	H <sub>2</sub>	+0.48	1950	Contact Potential	94	
"	H <sub>2</sub>	+1.12	1950	Photoelectric	105	
"	CO	+1.0	1959	Field Emission	66	70-80°K
"	CH <sub>4</sub>	+0.7	~ 1955	Field Emission	91	

Table 7 (Cont. )

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev. )	Year of Measurement	Method Used for Measurement	Reference	Remarks
W	Xe	-1.1	~ 1955	Contact Potential	107	Thin film
"	Xe	-1.38	1959	Field Emission	108	~80°K
"	Kr	-1.18	1959	Field Emission	108	~80°K
"	A	-0.87	1959	Field Emission	108	~80°K
"	A	-0.8	1959	Field Emission	109	
"	WO-Xe	-0.12	~1955	Contact Potential	107	
"	WO-O <sub>2</sub>	-0.04	~ 1955	Contact Potential	107	
Ni	O <sub>2</sub>	+1.40	~ 1950	Contact Potential	105	Filament, 293°K
"	O <sub>2</sub>	+0.55	1952	Contact Potential	110	
"	O <sub>2</sub>	+1.60	1950	Contact Potential	104	Thin film, 293°K
"	O <sub>2</sub>	+1.78	1939	Contact Potential	119	
"	CO	+1.38	~1957	Contact Potential	111	Thin film, -183°C
"	CO	+0.46	1954	Photoelectric	114	
"	CO	~+1.3	1957	Contact Potential	119	Thin film, 20°C
"	H <sub>2</sub>	~+0.1	1957	Photoelectric	113	Thin film, 293°C
"	H <sub>2</sub>	+0.12	1957	Photoelectric	114	Thin film, 293°C
"	H <sub>2</sub>	+0.35	1950	Contact Potential	104	Thin film, 293°C
"	H <sub>2</sub>	+0.35	~1957	Contact Potential	111	Thin film, 283°C
"	H <sub>2</sub>	+0.39	1956	Photoelectric	115	
"	H <sub>2</sub>	+0.40	1952	Contact Potential	110	

Table 7 (Cont.)

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev.)	Year of Measurement	Method Used for Measurement	Reference	Remarks
Ni	H <sub>2</sub>	~+0.5	1957	Field Emission	116	
"	H <sub>2</sub>	+0.35	~1950	Contact Potential	117	Thin film, ~-183-196°C
"	Xe	-0.85	~1955	Contact Potential	107	
"	Xe	-0.7	~1956		118	
"	Xe	-0.85	~1950	Contact Potential	117	Thin film
"	C <sub>2</sub> H <sub>4</sub>	-0.27	~1955	Contact Potential	107	
"	C <sub>2</sub> H <sub>4</sub>	-0.83	~1950	Contact Potential	117	
"	C <sub>2</sub> H <sub>4</sub>	-0.89	1954	Photoelectric	114	
"	C <sub>2</sub> H <sub>6</sub>	-0.77	~1950	Contact Potential	117	
"	C <sub>2</sub> H <sub>6</sub>	-0.23	~1957	Contact Potential	77	Thin film
"	C <sub>6</sub> H <sub>6</sub>	-1.3	~1957	Contact Potential	77	Thin film
"	C <sub>2</sub> H <sub>2</sub>	-0.21	~1957	Contact Potential	77	Thin film
"	C <sub>2</sub> H <sub>2</sub>	-1.0	1954	Contact Potential	117	
"	N <sub>2</sub>	-0.21	~1950	Contact Potential	117	
"	H-N <sub>2</sub>	-0.4	~1950	Contact Potential	117	
"	C <sub>2</sub> H <sub>4</sub> -H <sub>2</sub>	no change	~1950	Contact Potential	117	
"	C <sub>2</sub> H <sub>4</sub> -Xe	no change	~1950	Contact Potential	117	
Ta	H <sub>2</sub>	+0.44	1957	Photoelectric	113	Thin film, 293°K
"	H <sub>2</sub>	+0.43	1954	Photoelectric	114	Thin film, 293°K
"	N <sub>2</sub>	+0.38	1957	Photoelectric	113	Thin film, 293°K
"	CO	+0.67	1954	Photoelectric	114	Thin film, 293°K
Cu	Xe	-0.67	~1955	Contact Potential	107	Thin film

Table 7 (Cont. )

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev. )	Year of Measurement	Method Used for Measurement	Reference	Remarks
Cu	CO	-0. 30	~ 1957	Contact Potential	111	Thin film,-183°C
"	CO	-0. 30	1957	Contact Potential	119	Thin film,-293°K
"	H <sub>2</sub>	+0. 36	~ 1957	Contact Potential	111	Thin film,-183°C
"	H <sub>2</sub>	+0. 35	~ 1950	Contact Potential	106	
"	O <sub>2</sub>	+0. 68	1957	Contact Potential	119	Thin film,-293°K
"	N <sub>2</sub>	-0. 45	~ 1955	Contact Potential	107	Thin film
"	CH <sub>4</sub>	-0. 14	~ 1955	Contact Potential	107	Thin film
"	C <sub>2</sub> H <sub>4</sub>	-1. 23	~ 1955	Contact Potential	107	Thin film
"	C <sub>2</sub> H <sub>6</sub>	-0. 69	~ 1955	Contact Potential	107	Thin film
Fe	H <sub>2</sub>	+0. 19	1954	Photoelectric	114	Thin film,-293°K
"	H <sub>2</sub>	+0. 43	~ 1957	Contact Potential	111	
"	H <sub>2</sub>	+0. 47	1955	Contact Potential	120	Thin film, 293°K
"	CO	+1. 33	1957	Contact Potential	119	Thin film, 293°K
"	CO	+1. 64	~ 1957	Contact Potential	111	Thin film, 183°C
"	CO	+1. 15	1954	Photoelectric	114	Thin film, 293°K
"	Xe	-0. 66	~ 1955	Contact Potential	107	Thin film
"	Cl <sub>2</sub>	+1. 3	1961	Contact Potential	104	Maximum in-crease at ~200°C
"	I <sub>2</sub>	+0. 5	1961	Contact Potential	104	Maximum in-crease at ~20°C
Ag	H <sub>2</sub>	+0. 34	~ 1957	Contact Potential	111	Thin film,-183°C
"	H <sub>2</sub>	+0. 49	1950	Contact Potential	94	
"	H <sub>2</sub>	-0. 81	1935	Photoelectric	121	Probably contaminated

Table 7 (Cont. )

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev. )	Year of Measurement	Method Used for Measurement	Reference	Remarks
Fe	O <sub>2</sub>	+0.60	1952	Contact Potential	110	
"	O <sub>2</sub>	+1.2	1949	Contact Potential	122	
"	O <sub>2</sub>	+0.2	1959	Contact Potential	123	
"	CO	-0.31	~ 1957	Contact Potential	111	
"	N <sub>2</sub>	~ -0.2	1949	Contact Potential	122	
"	He	no change	1949	Contact Potential	122	
"	A	no change	1949	Contact Potential	122	
"	Halogens	+0.2 to +0.4	1935	?	124	
Au	H <sub>2</sub>	+0.18	~ 1957	Contact Potential	111	Thin film, -183°C
"	O <sub>2</sub>	+0.9 to +1.2	1953	Photoelectric	125	
"	CO	-0.93	~ 1957	Contact Potential	111	Thin film, -183°C
"	Halogens	+0.2 to +0.4	1935	?	124	
Hg	O <sub>2</sub>	-0.03	~ 1955	Contact Potential	107	
"	Xe	-0.23	~ 1955	Contact Potential	107	
"	CH <sub>4</sub>	-0.16	~ 1955	Contact Potential	107	
"	C <sub>2</sub> H <sub>2</sub>	-0.21	~ 1955	Contact Potential	107	
"	C <sub>2</sub> H <sub>4</sub>	-0.27	~ 1955	Contact Potential	107	
"	C <sub>2</sub> H <sub>6</sub>	-0.23	~ 1955	Contact Potential	107	
Pt	H <sub>2</sub>	-2.2	1935	Photoelectric	121	Probably Contaminated
"	O <sub>2</sub>	+1.2	1953	Photoelectric	124	
Co	H <sub>2</sub>	+0.33	~ 1957	Contact Potential	111	
"	H <sub>2</sub>	+0.06	1954	Photoelectric	114	Thin film



Table 7 (Cont. )

Substrate	Nature of Adsorbed Monolayer	Work Function Change (ev. )	Year of Measurement	Method Used for Measurement	Reference	Remarks
Co	H <sub>2</sub>	+0.31	1955	Contact Potential	120	Thin film, 293°K
"	CO	+0.26	1954	Photoelectric	114	Thin film
"	CO	+1.48	1954	Contact Potential	111	Thin film, -183°C
Ti	Xe	-0.84	~1955	Contact Potential	107	Thin film, 293°K
"	I <sub>2</sub>	+0.9	1954	Contact Potential	112	
"	Xe	-0.95	~1955	Contact Potential	107	
"	CO	+1.15	1957	Contact Potential	119	
Zn	Xe	-0.21	~1955	Contact Potential	107	Thin film, 293°K
"	CO	+0.08	1957	Contact Potential	119	
Pd	O <sub>2</sub>	+0.9 to +1.25	1953	Photoelectric	125	
K	Xe	no change	~1955	Contact Potential	107	Thin film, 293°K
Ca	Xe	no change	~1955	Contact Potential	107	Thin film, 293°K
Ba	O <sub>2</sub>	-0.32	1959	Contact Potential	127	Thin film, 293°K
Se	Xe	-0.1	~1955	Contact Potential	107	Thin film, 293°K
Ge	O <sub>2</sub>	+0.20	1957	Contact Potential	126	100 plane, 293°K
"	H <sub>2</sub>	-0.30	1957	Contact Potential	126	100 plane, 293°K
"	N <sub>2</sub>	-0.04	1957	Contact Potential	126	100 plane, 293°K
"	CO	+0.11	1957	Contact Potential	126	100 plane, 293°K
"	CO <sub>2</sub>	no change	1957	Contact Potential	126	100 plane, 293°K
Si	O <sub>2</sub>	+0.20	1948	Contact Potential	102	100 plane
Al	H <sub>2</sub>	+0.81	1935	Photoelectric	121	Probably contaminated

## 5. Low Work Function Materials

At the present time the main need for low work function materials, in the order of 1 ev., is for their use as collectors in thermionic energy converters, since lower work functions will result in higher efficiencies. Due to the fact that the lowest work function of an element in the periodic table is 1.89 ev. (cesium), the search for these substances, of necessity, involves mainly a study of compounds, particularly semiconductors, concerning which sufficient data is available to facilitate a basic approach to the problem. However, at the same time, it should be realized that the possibility exists of further utilizing the phenomena of monolayer adsorption upon surfaces, which was considered previously. Actually, it appears that in many cases both approaches have to be considered together in proposing possible mechanisms. In this section we will mainly consider a potential source of low work function materials that may be found in the work done on the development of semiconducting-type photoemitters. Examples of these emitters include those composed of the following constituents:  $\text{Ag-O-M}_x$ ,  $\text{Sb-M}_x$ ,  $\text{Sb-M}_x\text{M}_y$ ,  $\text{Bi-M}_x$ ,  $\text{Te-M}_x$ ,  $\text{Sb-M}_x\text{M}_y\text{M}_z$ ,  $\text{Bi-Ag-O-M}_x$ , etc., where  $\text{M}_x$ ,  $\text{M}_y$ ,  $\text{M}_z$  represent an alkali metal. Since information concerning the thermionic constants was found to be lacking in the majority of these solids, it was necessary to evaluate data obtained from photoelectric emission, photoconductivity, optical absorption measurements, and activation energies from a log conductivity versus  $1/T^\circ\text{K}$  plot. An analysis of the above data helps considerably in determining accurate values for the forbidden band gap,  $E_g$ , and the electron affinity,  $E_a$ , since the sum of these two parameters frequently give the threshold for photoelectric emission. Additional information concerning thermionic emission will, of course, locate the Fermi level and corroborate the values obtained for  $E_a$ .

Before continuing a discussion on the alkali photoemitters, it is well to consider low work function materials in general, where it has been established that the favorable parameters to be considered include low electron affinity, a very narrow band gap, or a sufficient concentration of donors (or defects) at an energy level close to the bottom of the conduction band - low temperatures also contribute to keeping the Fermi level above the donor level. At the

present time, the data on electron affinity which have been published in the literature appear to be fairly limited. One preliminary conclusion that has been reached is that ionic materials of large band gap often have low electron affinities. These materials may include alkali, alkaline earth and rare earth halides, oxides, among others. If it is true that ionic bond formation favors low electron affinities in the compound, the following parameters in a material might be considered important: large cation radius; efficient shielding by inner electrons with a resultant low effective nuclear charge; and a stable configuration of completely filled electronic shells in the resulting ion. In an analogous manner, a small radius, high effective nuclear charge, and a stable configuration favor ionic bond formation by a nonmetal.

However, it should be realized that the theoretical prediction of the bond gap energy also depends upon other parameters such as the bond energy, difference in electronegativities, electron affinity of the anion, interatomic distance in the unit cell, crystal structure, and electronic configuration. Thus it is seen that the prediction of the band gap width from first principles can be quite difficult. It is probably more apropos at the present time to observe the trends which occur in substances with similar electronic and crystal structures (14). For example, in Table 8 the electron affinities of  $\text{Na}_3\text{Sb}$ ,  $\text{K}_3\text{Sb}$ ,  $\text{Rb}_3\text{Sb}$ , (all hexagonal), and  $\text{Cs}_3\text{Sb}$  (cubic) appear to decrease quite markedly with the increasing atomic number of the alkali constituent.

If certain compounds which are to be considered as potential low work function materials possess large band gaps, it would appear that donor levels close to the conduction band would be essential if an extremely low  $\phi$  is to be obtained. The possible mechanism of the oxide coated cathode which has been described in Section 4 is an example of this; in alkali halides the creation of donor F centers which are correlated in some way with a nonstoichiometric excess of metal (replacing a negative ion at a vacant lattice site) is also favorable for the emission process (148).

In comparing thermionic and photoelectric emission it should be realized that although in a metal the thermionic and photoelectron work functions are identical and defined as the energy difference between the Fermi and vacuum level, in a semiconductor the photoelectric threshold is determined by the energy difference between the vacuum level and the energy

states with sufficiently high electron densities to produce appreciable photoemission. Usually, the maximum threshold for photoemission is considered to arise from the top of the valence band; however if the impurity levels are of sufficient concentration, (thereby absorbing a particular spectral wave length), they can provide the prime mechanism for emission. The more complex a compound, the more probable is it that impurity and defect levels may be the basis for photoemission, and a very careful analysis of the results must be undertaken before the mechanism can be accurately described. It is also generally assumed that in semiconductors the thermionic work function is always smaller than the photoelectric work function - this would be true primarily in the case of an intrinsic semiconductor, a semiconductor that is either heavily n doped or at a sufficiently low temperature that the Fermi level has not fallen below the donor level, and a p type material that probably has a small excess of acceptors over donors and is at a sufficiently high temperature so that the Fermi level is raised above the acceptor level (see Section 4).

Looking at the alkali photoemitters which are shown in Table 8 it is well to consider that these semiconductors may be complex even in the case where only two components are present. Most likely donor levels as well as acceptor levels are present, and the excess of one over the other determines the conductivity. These materials appear to be quite structure and surface sensitive; a slight amount of contamination on the surface appears to cause a considerable change in properties, particularly those pertaining to the electron affinity (formation of a favorable or unfavorable dipole layer). Since photoemitters are thin films, surface irregularities and structural defects will affect the electrical properties to a greater extent than when bulk materials are considered. Also, since the surface of a semiconductor is usually not electrically neutral, the dipole layer or space charge region is a considerable percentage of the entire thickness of the film. The exact preparation of these materials is quite critical (133) and even the amount of contamination due to a poor vacuum can have considerable effect upon the desired properties - it could enhance the photoemission as well as decrease it.

The crystal structures for the majority of these substances are either face-centered or  $\text{Na}_3\text{As}$ -type hexagonal with the former tending to give

lower photoelectric work functions than the latter due largely to a decrease in the electron affinity. The cubic structures appear to possess p conductivity, while those with the hexagonal structure have n conductivity (129). This difference has been attributed to the fact that the lattice spacings in the hexagonal structure are such that excess interstitial alkali atoms may fit into the lattice; whereas for the cubic structures, interstitials may not only be prohibited but vacant alkali sites may act as acceptors. It is also possible that donor and acceptor type impurities or defects at the surface (surface states) affect the work function by introducing additional energy levels in the forbidden band gap. This effect seems to be caused by the bending of the conduction and valence bands in certain cases. The bands will bend in such a direction as to make the Fermi level at the surface coincide with that of the bulk and is due to the space charge or dipole layer caused by the transfer of charge from the surface. If smaller work functions are desirable, the bands should move downward; this can most readily occur with an n-type layer existing at the surface of a p-type layer. The space-charge layer contains a net negative charge which counterbalances the positive charge remaining on the surface. The experimentally determined electron affinities seem to be larger for the n-type films than those possessing hole conductivity and this is the trend which might be expected if band bending were taking place. In the case of  $\text{Cs}_3\text{Sb}$  which is hole conducting, experimental results have shown that with a sufficiently high partial pressure of cesium vapor, the compound, can be driven through a conductivity minimum and become n-type; however when the cesium pressure is removed, the excess cesium leaves the  $\text{Cs}_3\text{Sb}$  and the material returns to p-conductivity. Excess cesium deposited on the surface of the  $\text{Cs}_2\text{O}$  layer in a  $[\text{Ag}] - \text{Cs}_2\text{O}$  cathode also appears to give up electrons to the lattice thereby causing a decrease in the surface potential (31). Sommer (136) also came to the conclusion Cs added to  $(\text{NaK})_3\text{Sb}$  only reduces the electron affinity and does not affect the bulk properties of the material. The exact work functions that are obtained are due to the amount of excess cesium and the extent of the possible competing reactions that may be taking place at the surface. The possibility of the formation of extremely complex semiconductive layers at the surface of most photoemitters should not be overlooked.

In Table 8 various data pertinent to these photoemitters are shown. With regards to values listed for the band gaps it should be emphasized again that these values may in some cases represent the energy levels from the defect or impurity bands instead of the valence band. With regards to the thermionic work function it is the location and concentration of these levels that will help determine the location of the Fermi levels as well as an indication of its possible temperature dependence.

In predicting future materials that might offer a possibility for fruitful investigation it is necessary to consider the possible effect that the various parameters mentioned in this section may have on the values for the band gap, electron affinity, and impurity levels. For example, the electron affinities of group IA-VIB compounds do not appear to have been determined at the present time, but there are indications that they may be smaller than those of the antimonides due, among other factors, to the greater ionic character and smaller negative anion radius in the I-VI group. It also appears to be possible to bring about considerable changes in the properties of  $\text{Cs}_3\text{Sb}$  by the formation of alloys of Sb with substances such as In and Tl. Certainly, countless ternary and quaternary combinations are possible in the synthesis of new compounds from groups such as IA-VB, IA-VIB, IIA-VB, etc.

It is seen from this discussion that the problem of selecting favorable materials for use as low work function collectors and of developing their optimum properties go hand in hand.

TABLE 8  
SUMMARY OF DATA FOR SOME ALKALI PHOTOEMITTERS

Material	Photoelectric Work Function (ev.)	Thermionic Work Function (ev.)	Band Gap (ev.)	Electron Affinity (ev.)	Crystal Structure	Conductivity Type	Reference
Na <sub>3</sub> Sb	3.1 - 3.5	-	1.1	2.0-2.4	hexagonal	n	128, 129
KSb	2.2 - 2.9	-	0.9	-	-	-	130
K <sub>3</sub> Sb	-	-	1.1	1.1-1.8	hexagonal	n	128, 129
"	-	-	0.8	-	-	-	130
"	-	-	-	0.6	hexagonal	-	131
"	1.7	-	~1.0	0.7	-	-	128, 129
CsSb	-	-	~0.8	-	-	-	130
Cs <sub>3</sub> Sb	2.05	-	1.6	0.45	cubic	p	128, 129
"	-	-	-	0.4	-	-	131
"	-	-	0.5-0.6	-	-	-	130
"	1.8-1.9	1.2-1.6	-	-	-	p	132
"	-	1.2	1.7	-	-	-	134
"	-	1.65	-	-	-	-	133
"	-	1.3-1.5	-	-	-	-	135
CsSn	~1.9	-	-	-	-	p	132
Cs <sub>x</sub> Te	-	1.2	-	-	-	-	135

TABLE 8 (Cont'd)

Material	Photoelectric Work Function (ev.)	Thermionic Work Function (ev.)	Band Gap (ev.)	Electron Affinity (ev.)	Crystal Structure	Conductivity Type	Reference
Cs <sub>2</sub> Te	-	-	~3.5	-	-	-	133
Cs <sub>2+x</sub> Te	-	-	~1.5	-	-	-	133
Cs <sub>3</sub> Bi	~2.0	-	≤0.7	≥1.3	cubic	-	136
"	1.6-1.7	~1.6	0.5-0.7	0.9-1.1	-	-	136
"	-	-	0.5-0.6	-	-	-	130
Cs <sub>3</sub> Bi(0)	1.7	-	≤0.7	≥1.0	-	-	136
Cs <sub>3</sub> Bi(Ag)	2.0	-	≤0.7	≥1.0	-	-	136
Cs <sub>3</sub> Bi(0)(Ag)	1.6	-	≤0.7	≥0.9	-	-	136
Rb <sub>3</sub> Sb	-	-	1.0	1.2	hexagonal	n	128, 129
Rb <sub>2</sub> Te	-	-	~4.5	-	-	-	133
Rb <sub>2+x</sub> Te	-	-	~2.5	-	-	-	133
Na <sub>2</sub> KSb	-	-	1.0	1.0	cubic	p	128, 129
[Rb]Na <sub>2</sub> KSb	-	-	1.0	0.7	cubic	p	128, 129
[Cs]Na <sub>2</sub> KSb	-	-	1.0	0.55	cubic	-	128, 129
[Ag]-Cs <sub>2</sub> O	0.95	0.75	-	-	cubic	p	137
"	0.80-0.96	0.75-0.86	-	-	-	-	138



TABLE 8 (Cont'd)

Material	Photoelectric Work Function (ev.)	Thermionic Work Function (ev.)	Band Gap (ev.)	Electron Affinity (ev.)	Crystal Structure	Conductivity Type	Reference
[Ag]-Cs <sub>2</sub> O	0.91	0.75	-	-	-	-	139
"	1.06	0.92	-	-	-	-	140
"	-	0.37	-	-	-	-	141
"	0.95	0.6	-	-	-	-	142
"	0.88	-	-	-	-	-	143
"	1.00	-	-	-	-	-	144
"	-	0.74	-	-	-	-	145
"	0.95-1.12	-	-	-	-	-	146
"	0.99	0.94	-	-	-	-	147
"	1.06	0.83	-	-	-	-	31

## 6. Summary

This report has been concerned with a study of the solid state properties of materials and the particular factors which affect the work function and its temperature coefficient of metals, semiconductors, and insulators. The specific basic parameters that were investigated included electron affinity, band gap, energy bulk, impurity or defect levels, dipole or space charge layer at the surface, existence of donor or acceptor type surface states, Fermi level and its temperature dependence, band bending, etc. The contribution of the work function of individual crystallographic planes to the total work function of a polycrystalline material was found to be considerable.

Among the areas least understood is that involving the influence of the surface upon the work function. Both the dipole layer inherently present at a surface and the changes induced in the layer by adsorbed gases or surface impurities were found to play a major role. A study was made of the possible mechanisms involved in the electronic interactions which result from the adsorption on a surface of partially complete monomolecular films. One correlation of sorts was found to exist in certain cases between the work function changes caused by an adsorbed gas and the difference in electronegativity or degree of ionicity between the gas and the substrate. In connection with surface studies a table was compiled of the vast majority of published adsorption data found in the literature.

Finally, a study was initiated of the principles governing the work function of semiconductors which are potentially useful low work function collector materials. One group of interesting compounds was found to be those concerned with the development of semiconducting type photoemitters, namely those composed of various combinations of alkali metals with groups IB and VB elements or their oxides. Parameters such as crystal structure, type of defect, degree of ionicity, bond energy, etc. were found to have a marked effect on the electron affinity and the magnitude of the forbidden band gap.

It is expected that during 1963 the main emphasis of this program will continue to be directed toward prediction of work functions of materials of interest for thermionic converters and toward the corollary problem, the

suggestion of materials with particular values of the work function and other physical and chemical properties which are desired for efficient thermionic converters. Such predictions and suggestions depend upon the continued effort towards correlation with other solid state, physical, and structural properties of classes of materials. Beyond this, however, prediction of performance will depend upon the ability to predict how surface effects may be altered by preparative techniques and by exposure to particular environments.

## REFERENCES

1. Suhrmann, R. and Schallmanach, A. , Zeitschr. f. Physik 91, 775, (1929).
2. DuBridge, L. A. and Roehr, W. W. , Phys. Rev. 43, 428, (1933).
3. Fowler, R. H. , Phys. Rev. 38, 45, (1931).
4. Cardwell, A. B. , Phys. Rev. 47, 628, (1935).
5. Krueger, F. and Stabenow, G. , Ann. Phys. 22, 713, (1935).
6. Waterman, A. T. and Potter, J. G. , Phys. Rev. 51, 63, (1937).
7. Reimann, A. L. , Proc. Roy. Soc. (A) 163, 499, (1937).
8. Potter, I. G. , Phys. Rev. 58, 623, (1940).
9. Herzfield, K. F. , Phys. Rev. 35, 248, (1930).
10. Blochinzer, D. and Drabkina, S. , Physik Zeits Sowfetunion 7, 484, (1935).
11. Reimann, A. L. , Nature 133, 833, (1934).
12. Seely, S. , Phys. Rev. 59, 75, (1941).
13. Wigner, E. P. , Phys. Rev. 46, 509, (1934).
14. Goodman, P. and Homonoff, H. , Summary Report No. 1, Study of Materials for Thermionic Converters, 31 Dec. 1961, Contract No. Nonr-3385(00) Task No. NR099-355.
15. Sun Nein Tai and Band, W. , Proc. Camb. Phil. Soc. 42, 72, (1946).
16. Wohlfahrt, E. P. , Proc. Phys. Soc. 60, 360 (1948).
17. Wigner, E. and Bardeen, D. , Phys. Rev. 48, 84, (1935).
18. Herring, C. and Nichols, M. H. , Revs. Mod. Phys. 21, 248, (1949).
19. Rose, B. A. , Phys. Rev. 44, 585, (1933).
20. Martin, S. T. , Phys. Rev. 56, 947, (1939).
21. Nichols, M. H. , Phys. Rev. 57, 297, (1940).

21. Nichols, M.H. , Phys. Rev. 57, 297, (1940).
22. Smith, G.F. , Phys. Rev. 94, 295, (1954).
23. Müller, E.W. , J. Appl. Phys. 26, 732, (1955).
24. Smoluchowski, R. , Phys. Rev. 60, 661, (1941).
25. Hutson, A.R. , Phys. Rev. 98, 889, (1955).
26. Crowell, C.R. , and Armstrong, R.A. , Phys. Rev. 114, 1500, (1959).
27. Blevis, E.H. , and Crowell, C.R. , Bull. Amer. Phys. Soc. Series II 5, 347, (1960).
28. Shockley, W. , Electrons and Holes in Semiconductors, (D. Van Nostrand Company, Inc. , N. Y. , 1950).
29. Wilson, A.H. , Proc. Roy. Soc. 134, 277 (1931).
30. Fowler, R.H. , Statistical Mechanics, (Cambridge Press, London, 1936).
31. Davey, J.E. , J. Appl. Phys. 28, 1031, (1957).
32. Hensley, E.B. , J. Appl. Phys. 32, 301 (1961).
33. DuPré, F.K. , Hutner, R.A. , and Rittner, E.S. , Phys. Rev. 78, 567 (1950).
34. Bardeen, J. , Phys. Rev. 71, 717 (1947).
35. Bondarenko, B.V. , Fiz Tverdogo Tela 2, 2140, (1960).
36. Huber, H. and Wagener, S. , Z. Tech. Physik. 23, 1 (1942).
37. Sparks, I.L. , Ph.D. Thesis, (Univ. of Missouri), (1951).
38. Cusak, N. , The Electrical and Magnetic Properties of Solids, (Longmans, Green and Co. N. Y. , 1958), p. 227.
39. deBoer, J.H. , Advances in Catalysis, 8, 17, (1956).
40. London, F. , Z. Physik, 63, 245, (1930).
41. Slater, J.C. and Kirkwood, J.G. , Phys. Rev. , 37, 682 (1931).
42. Müller, A. , Proc. Roy. Soc. (London) A154, 624, (1936).

43. Born, M. and Mayer, J. E. , Z. Physik, 75, 1 (1932).
44. Polanyi, M. and London, F. , Naturwissenschaften 18, 1099, (1930).
45. Lennard-Jones, J. E. , Trans. Faraday Soc. 28, 333, (1932).
46. Bardeen, J. , Phys. Rev. 58, 72, (1940).
47. Margenau, H. and Pollard, W. G. , Phys. Rev. , 103, 597, (1956).
48. Ehrlich, G. and Hudda, F. G. , J. Chem. Phys. 28, 493, (1959).
49. Mulliken, R. S. , J. Am. Chem. Soc. 74, 811, (1952).
50. Pauling, L. , The Nature of the Chemical Bond, 3rd Edition (Cornell Univ. Press, Ithaca, N. Y. , 1960).
51. Dowden, D. A. , J. Am. Chem. Soc. 72, 242 (1950).
52. Gurney, R. W. , Phys. Rev. 47, 479 (1935).
53. Higuchi, I. , Ree, T. and Eyring, H. , J. Am. Chem. Soc. 79, 1330, (1957).
54. Drechsler, M. , Z. Elektrochem 58, 334, (1954).
55. Langmuir, I. and Taylor, J. , Phys. Rev. 44, 423, (1933).
56. Eley, D. D. , Disc. Faraday Soc. 8, 34 (1950).
57. Roberts, J. K. , Some Problems in Adsorption (Cambridge Press, New York, 1939).
58. Ehrlich, G. and Hudda, F. G. , J. Chem. Phys. 35, 1421, (1961).
59. Taylor, J. B. and Langmuir, I. , Phys. Rev. 40, 463, (1932).
60. Langmuir, I. and Kingdon, K. A. , Phys. Rev. 34, 129, (1929).
61. Mayer, H. and Ann. Physik 33, 419, (1938).
62. Wright, D. A. , Proc. Inst. Elec. Engrs. Part III, Vol. 100 (1953).
63. Becker, J. A. , Trans. Faraday Soc. 28, 148 (1932).
64. Moore, G. E. and Allison, H. W. , J. Chem. Phys. 23, 1609, (1955).

65. Zingerman, Y. P., Ishchuk, V. A., Morozowski, U. A., Soviet Phys. Solid State 3, No. 4, Oct. (1961).
66. Hayward, D. O. and Gomer, R., J. Chem. Phys. 1617, (1959).
67. Gavriluk, V. M., Bull. Acad. Sci. USSR Phys. Ser. 20, 967, (1956).
68. Ryde, I. W. and Harris, N. L., quoted by Reimann, A. L., Thermionic Emission, p. 159 (1934).
69. Reimann, A. L., Proc. Roy. Soc. (London) A163, 499, (1937).
70. Bosworth, R. C. L. and Rideal, E. K., Proc. Roy. Soc. (London) A162, 1, (1937).
71. Aämodt, R. L., Brown, L. J. and Nichols, B. D., Power Information Center Thermionic Conference - December 1961, ASTIA-AD 270905.
72. Missman, R. A. and Pidd, R. W., Power Information Center Thermionic Conference - December 1961, ASTIA-AD 270905.
73. Haefer, R. Z. Physik 116, 604, (1940).
74. Brattain, W. H. and Becker, J. A., Phys. Rev. 43, 428, (1933).
75. Gallagher, C. J., Phys. Rev. 65, 46, (1944).
76. Ives, H. E., and Olpin, A. R., Phys. Rev. 34, 117, (1929).
77. Eley, D., and Rideal, E. K., Proc. Roy. Soc. (London) A178, (1941).
78. Reimann, A. L., Phil Mag. (7) 20, 594, (1935).
79. Klein, R., J. Chem. Phys. 21, 1177 (1953).
80. Copley, M. J. and Spence, R. W., J. Am. Chem. Soc. 61, 3027 (1939).
81. Bosworth, R. C. L., and Rideal, E. K., Proc. Roy. Soc. (London) A162, 1, (1937).
82. Bourion, R., J. Phys. Radium 12, 930 (1951).
83. Mignolet, J. C. P., Rec. Trav. Chim 74, 685, (1955).
84. Gomer, R. and Hulm, J. R., J. Chem. Phys. 27, 1363, (1957).

85. Morgulis, N. D. and Naumovets, Izv. Akad. Nauk. SSSR set fiz. 24, 647, (1960).
86. Bosworth, R. C. L. and Rideal, E. K., Physica 4, 925, (1937).
87. Ehrlich, L. and Hudda, F. L., J. Chem. Phys. 35, 1421, (1961).
88. Suhrmann, R. Z., Elektrochem 60, 804, (1956).
89. Eisinger, J., J. Chem. Phys. 28, 165, (1958).
90. Ehrlich, L., Hickmott, T. W., and Hudda, F. L., J. Chem Phys. 28, 506, (1958).
91. Becker, J. A., Solid State Phys., Vol. 7, 400, (1958).
92. Jones, P., and Pethica, B., Proc. Roy. Soc. (London) A256, 454, (1960).
93. Shrednick, V. N. Izv. Akad. Nauk SSSR Ser. Fiz 22, 594, (1958).
94. Mignolet, J. C. P., Disc. Faraday Soc. 8, 326, (1950).
95. Eisinger, J., J. Chem. Phys. 27, 1206 (1957).
96. Klein, R., J. Chem. Phys. 31, Nov. (1959).
97. Oatley, C. W., Proc. Phys. Soc. (London) 51, 318, (1939).
98. Mignolet, J. C. P., J. Chem. Phys. 20, 341 (1952).
99. Mignolet, J. C. P., J. Chem. Phys. 47, 172, (1950).
100. Gomer, R., Wortman, R. and Lundy, R., J. Chem. Phys. 26, 1147, (1957).
101. Bosworth, R. C. L., Proc. Camb. Phil. Soc. 33, 394, (1937).
102. Weissler, L. L., and Wilson, T. N., Phys. Rev. 73, 538, (1948).
103. Eberhagen, A., Fortschr Physik 8, 245, (1960).
104. Popova, L. Shutmovshaya et al, Doklady, Akad. Nauk SSSR 137, No. 4, (1961).
105. Bosworth, R. C. L. Trans. Faraday Soc. 8, 105 (1950).



106. Schlier, E. and Farnsworth, H. E. , Phys. Rev. 78, 316 (1950).
107. Mignolet, J. C. P. in Chemisorption, (Butterworths, London, edited by W. E. Garner, 1956).
108. Ehrlich, L. and Hudda, F. L. , J. Chem. Phys. 10, No. 2, February 1959.
109. Gomer, R. , J. Phys. Chem. 63, 468, 1959.
110. Ogawa, L. , Doke, T. , and Nakada, I. , J. Appl. Phys. (Japan) 21, 223, 1952).
111. Culver, R. V. , Pritchard, J. , and Tompkins, F. C. , Proc. 2nd Intern Congr. on Surface Activity, Vol. 2 (Butterworths, London, 1957).
112. Malamud, H. and Krumbein, A. D. , J. Appl. Phys. 25, 591, (1954).
113. Sachtler, W. M. H. , and Dorgelo, G. J. H. , J. Chem. Phys. 54, 27, (1957).
114. Baker, M. and Rideal, E. K. , Nature 174, 1185, (1954).
115. Suhrmann, R. , Z Elektrochem 60, 804, (1956).
116. Wortman, R. , Gomer, R. , and Lundy, J. Chem. Phys. 27, 1099, (1957).
117. Rideal, E. , Disc. Faraday Soc. (Heterogeneous Catalysis) 8, 1950.
118. Suhrmann, R. , Symposium on the Surface Reactions of Gases on Metals (Paris, France, May, 1956).
119. Bloyaert, F. , D'Or, L. , and Mignolet, J. C. P. , J. Chem. Phys. 54, 53, (1957).
120. Mignolet, J. C. P. Bull. Soc. Chem. Belg. 64, 126, (1955).
121. Suhrmann, R. and Csech, Z. Physik Chem. (Liepzig) B28, 215, (1935).
122. Weissler, L. L. and Wilson, T. N. , Phys. Rev. 76, 591, (1949).
123. Kummer, J. T. , J. Phys. Chem. 63, 460, (1959).
124. Oullet, C. and Rideal, E. K. , J. Chem. Phys. 3, 150, (1935).

125. Giner, J. and Lange, E., *Naturwiss.* 40, 506, (1953).
126. Dillon, J. A. and Farnsworth, H. E., *J. Appl. Phys.* 28, 174, (1957).
127. Anderson, P. A. and Hunt, A. L., *Phys. Rev.* 115, 550, (1959).
128. Spicer, W. E., *Phys. Rev.* 112, 114, (1958).
129. Spicer, W. E., *J. Appl. Phys.* 31, 2077, (1960).
130. Pincherle, L. and Radcliff, M., *Adv. In Phys.* 5, 271, (1956).
131. Taft, E. A. and Philipp, H. R., *Phys. Rev.* 115, 1583, (1959).
132. Sakata, T., *J. Phys. Soc. Japan* 8, 723, (1953).
133. Görlich, P., *Adv. in Electronics and Electron Physics*, (Academic Press, N. Y., 1959).
134. Eckart, F., *Ann. Physik* 19, 133 (1956).
135. Chapman, R. A., *et al*, First Summary Report, November 1962, Contract Nonr. 3705(00) fbm from Texas Instruments, Inc. ASTIA AD 290955.
136. Sommer, A. H. and Spicer, W. E., *J. Appl. Phys.* 32, 1036, (1961).
137. Koller, L. R., *Phys. Rev.* 33, 1082, (1929).
138. Görlich, P., *Z. Physik* 116, 704, (1940).
139. Asao, S., *Proc. Phys., Math Soc. Japan*, 22, 448, (1940).
140. Eckart, F., *Ann. Physik* 16, 323, (1955).
141. Kingsbury, E. F. and Stilwell, G. R., *Phys. Rev.* 37, 1549 (1931).
142. Campbell, N. R., *Phil. Mag.* 12, 174 (1931).
143. DeBoer, J. H. and Teves, M. C., *Z. Physik* 83, 521, (1933).
144. Prescott, C. H., Jr. and Kelly, M., *J. Electrochem. Soc. Trans.*, 62, 297, (1932).
145. Rajchmann, J., Thesis, Zurich, 1938.
146. Fleischer, R. and Görlich, P., *Z. Physik* 35, 289 (1934).

147. Lallemand, A. and Duchesne M., Z. Angew, Math. U. Physik 1, 195, (1950).
148. Mott, N. F. and Gurney, R. W. , Electronic Process in Ionic Crystals, 2nd Edition, (Oxford Press, London, 1948).
149. Sommer, A. H. , Rev. Sci. Instr. 26, 725, (1955).

### Acknowledgement

The authors are indebted to Drs. S. Koslov, B. Sellers, and P. Goodman for encouragement and assistance.

## MASTER DISTRIBUTION LIST

### 099-Energy Conversion

	<u>No. copies</u>
Office of Naval Research Power Branch (Code 429) Department of the Navy Washington 25, D. C.	4
Cognizant ONR Area Branch Office	1
U. S. Naval Research Laboratory Technical Information Division Washington 25, D. C.	6
Commanding Officer Office of Naval Research Branch Office Box 39 Navy #100 Fleet Post Office New York, New York	2
Office of Technical Services Department of Commerce Washington 25, D. C.	1
Armed Services Technical Information Agency Arlington Hall Station Arlington 12, Virginia	10
National Aeronautics & Space Administration 1520 H. Street, N. W. Washington 25, D. C. Attn: James J. Lynch	1
National Aeronautics & Space Administration Lewis Research Center 2100 Brookpark Road Cleveland 35, Ohio Attn: Frank Rom Roland Breitwieser Bernard Lubarsky	1 1 1
Chief of Naval Operations (OP-07G) Department of the Navy Washington 25, D. C.	1
Commandant, U. S. Marine Corps Code CSY-3 Headquarters, Marine Corps Washington, 25, D. C.	1

	<u>No. copies</u>
Chief, Bureau of Ships Department of the Navy Washington 25, D. C.	
Attn: Code 342B	2
Code 1500, Mr. Wm. Hewitt	1
Code 456B, Mr. V. Gardner	1
Code 335	2
U. S. Atomic Energy Commission Division of Reactor Development Washington 25, D. C.	
Attn: Auxiliary Power Branch	1
Direct Conversion Branch	1
Army Reactor & Water Systems Branch	1
U. S. Atomic Energy Commission San Francisco Operation Office 2111 Bancroft Way Berkeley 4, California	
Attn: Reactor Division	1
Aeronautical Systems Division ASRMFP-2 Wright Patterson Air Force Base Ohio	
	1
Air Force Cambridge Research Center (CRZAP) L. G. Hanscom Field Bedford, Massachusetts	
	1
Power Information Center University of Pennsylvania Moore School Building 200 South 33rd Street Philadelphia 4, Pennsylvania	
	1
Director of Special Projects (SP-001) Department of the Navy Washington 25, D. C.	
	1
Los Alamos Scientific Laboratory P. O. Box 1663 Los Alamos, New Mexico	
Attn: Dr. George M. Grover	1
Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois	
Attn: Aaron J. Ulrich	1

	<u>No. copies</u>
Director, Advanced Research Projects Agency The Pentagon Washington 25, D. C. Attn: Dr. John Huth	1
U. S. Army Signal R & D Laboratory Fort Monmouth, New Jersey Attn: Emil Kittl	1
Mr. A. F. Underwood Manager, General Motors Research Labs. 12 Mile and Mound Road Warren, Michigan Attn: Dr. F. Jamerson	1
Atomics International P. O. Box 309 Canoga Park, California Attn: Dr. R. C. Allen	1
General Atomic P. O. Box 608 San Diego 12, California Attn: Dr. W. Pidd	1
ARACON Laboratories Virginia Road Concord, Massachusetts Attn: Dr. S. Ruby	1
Ford Instrument Company 3110 Thomson Avenue Long Island City, New York Attn: T. Jarvis	1
Armour Research Foundation 10 W. 35th Street Chicago 16, Illinois Attn: Dr. D. W. Levinson	1
Jet Propulsion Laboratory California Institute of Technology 4800 Oak Grove Drive Pasadena, California	1
RCA Laboratories David Sarnoff Research Center Princeton, New Jersey Attn: Dr. Paul Rappaport	1

	<u>No. copies</u>
The Martin Corporation Baltimore 3, Maryland Attn: Dr. M. Talaat	1
Thermo Electron Engineering Corporation 85 First Avenue Waltham 54, Massachusetts Attn: Dr. George Hatsopoulos	1
Hughes Research Laboratories 3011 Malibu Canyon Road Malibu, California Attn: Dr. R. C. Knechtli	1
Thomson Ramo Wooldridge, Inc. 7209 Platt Avenue Cleveland 4, Ohio Attn: Wm. J. Leovic	1
General Electric Research Laboratory Schenectady, New York Attn: Dr. V. C. Wilson	1
The Marquardt Corporation ASTRO Division 16555 Saticoy Street Van Nuys, California Attn: A. N. Thomas	1
Texas Instruments, Inc. P. O. Box 5474 Dallas 22, Texas Attn: Dr. R. A. Chapman	1
University of Denver Colorado Seminary Denver Research Institute Denver 10, Colorado Attn: Dr. Charles B. Magee	1
Radio Corp. of America Electron Tube Division Lancaster, Pennsylvania Attn: F. G. Block	1
Electro Optical Systems Inc. 125 N. Kinedo Avenue Pasadena, California Attn: A. Jensen	1



	<u>No. copies</u>
General Electric Company P. O. Box 846 Atomic Product Division Vallecitos Laboratory Pleasanton, California Attn: Robert Scott	1
General Electric Company Power Tube Division 1 River Road Schenectady 5, New York Attn: Mr. Wm. Miller	1
Consolidated Controls Corporation Bethel, Connecticut Attn: Mr. David Mends	1
Institute for Defense Analysis 1666 Connecticut Avenue, N. W. Washington, D. C. Attn: Mr. Robert Hamilton	1

<p>Abstract Contract Nonr -3385(00)</p> <p>ARACON Laboratories, a division of Allied Research Associates, Inc. - "STUDY OF MATERIALS FOR THERMIONIC CONVERTERS." Harold Homonoff, Stanley Ruby, (83 pages).</p> <p>A summary is presented in this second report of the theoretical study concerning materials for use in thermionic converters. Of those properties required for satisfactory long-lived performance of a material as either the emitter or collector, it was considered that the work function was most critical. Factors relating to the crystalline structure, surface, and adsorption phenomena, and the electronic nature of interatomic interactions, are discussed for the following classes of materials.</p> <ul style="list-style-type: none"> <li>A. Metals</li> <li>B. Ionic Solids</li> <li>C. Semiconductors</li> </ul>	<p>Abstract Contract Nonr -3385(00)</p> <p>ARACON Laboratories, a division of Allied Research Associates, Inc. - "STUDY OF MATERIALS FOR THERMIONIC CONVERTERS." Harold Homonoff, Stanley Ruby, (83 pages).</p> <p>A summary is presented in this second report of the theoretical study concerning materials for use in thermionic converters. Of those properties required for satisfactory long-lived performance of a material as either the emitter or collector, it was considered that the work function was most critical. Factors relating to the crystalline structure, surface, and adsorption phenomena, and the electronic nature of interatomic interactions, are discussed for the following classes of materials.</p> <ul style="list-style-type: none"> <li>A. Metals</li> <li>B. Ionic Solids</li> <li>C. Semiconductors</li> </ul>
<p>Abstract Contract Nonr -3385(00)</p> <p>ARACON Laboratories, a division of Allied Research Associates, Inc. - "STUDY OF MATERIALS FOR THERMIONIC CONVERTERS." Harold Homonoff, Stanley Ruby, (83 pages).</p> <p>A summary is presented in this second report of the theoretical study concerning materials for use in thermionic converters. Of those properties required for satisfactory long-lived performance of a material as either the emitter or collector, it was considered that the work function was most critical. Factors relating to the crystalline structure, surface, and adsorption phenomena, and the electronic nature of interatomic interactions, are discussed for the following classes of materials.</p> <ul style="list-style-type: none"> <li>A. Metals</li> <li>B. Ionic Solids</li> <li>C. Semiconductors</li> </ul>	<p>Abstract Contract Nonr -3385(00)</p> <p>ARACON Laboratories, a division of Allied Research Associates, Inc. - "STUDY OF MATERIALS FOR THERMIONIC CONVERTERS." Harold Homonoff, Stanley Ruby, (83 pages).</p> <p>A summary is presented in this second report of the theoretical study concerning materials for use in thermionic converters. Of those properties required for satisfactory long-lived performance of a material as either the emitter or collector, it was considered that the work function was most critical. Factors relating to the crystalline structure, surface, and adsorption phenomena, and the electronic nature of interatomic interactions, are discussed for the following classes of materials.</p> <ul style="list-style-type: none"> <li>A. Metals</li> <li>B. Ionic Solids</li> <li>C. Semiconductors</li> </ul>